THE EFFECT OF DISPERSION TECHNIQUES ON FRACTURE TOUGHNESS OF NANOCOMPOSITES PREPARED USING XG M-5 GRAPHENE NANOPLATELETS AND EPON 862 EPOXY RESIN

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Abstract: This investigation reports on the effects of various mechanical dispersion techniques, surface treatments, and coupling agents on the fracture toughness of an epoxy resin reinforced with graphene nanoplatelets. The epoxy resin selected is Diglycidyl ether of bisphenol F (DGEBF). The graphene nanoplatelets are 99.5% pure graphene and added to the epoxy resin in an amount ranging from 0.1 to 2.0 wt.%. Ultrasonication and ball milling are used as high energy mixing processes for breaking up the aggregates of graphene nanoplatelets. Subsequently, ball milled graphene nanoplatelets are dispersed in solvents using ultrasonication and then added to the epoxy resin. A non-ionic surfactant that has a hydrophilic polyethylene oxide chain (on average it has 9.5 ethylene oxide units) and an aromatic hydrocarbon lipophilic or hydrophobic group where the hydrocarbon group is a 4-(1,1,3,3-tetramethylbutyl)-phenyl group (also known as Triton X-100) is used along with two different types of silanes, namely 3-glycidoxy-propyl-trimethoxy silane (GPTMS) and 3-amino-propyl-trimethoxy silane (APTMS) are chosen. Triton X-100 is 4-(1,1,3,3-Tetramethylbutyl) phenyl-polyethylene glycol. GPTMS and APTMS chains graft on GnP surface and take part in covalent bond formation with the epoxy matrix. FTIR spectroscopy is used to evaluate the effects of chemical functionalization of graphene nanoplatelets and fracture toughness measurements are carried out using ASTM D5045. Spectral lines from FTIR analysis show us presence of covalent bonds between silane functional groups grafted on the surface of graphene nanoplatelets and epoxy groups after sample has been processed. ASTM D5045 test results show highest fracture toughness values for 1.0 wt.% samples processed using 3-amino-propyl-trimethoxy silane (APTMS) when compared to other samples. The modified samples had the highest fracture toughness values. SEM images show agglomerations forming when no modification technique was used. All other samples had considerably less visible aggregation sites. All these show that modifications techniques used for dispersion of graphene nanoplatelets in epoxy do work and it improves fracture toughness values while reducing aggregation of graphene nanoplatelets.

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CHAPTER I

INTRODUCTION

Epoxy resins are widely used polymers that find various applications due to their highly useful mechanical and physical properties. These good properties of epoxy are due to the high degree of chemical cross-linking. However, this high degree of chemical cross-linking makes the epoxy resin brittle and hence exhibit low resistance against crack propagation. In order to enhance the fracture resistance, researchers have used different types of nano and micro scale filler materials such as clay, carbon nanotubes (CNTs), rubber, POSS, graphene, etc. These reinforcing fillers showed promising results in improving fracture toughness. However, these nano scale fillers tend to form agglomerates at lower loading and these become the critical site of failure. Graphene due its unique properties have attracted various studies. Graphene is a single layer of carbon atoms packed densely in a honeycomb crystal lattice structure. Graphene nanoplatelets are used as filler materials in epoxy resins for manufacturing nanocomposites due to their interesting and useful properties. Graphene nanoplatelets display superior mechanical properties along with high electrical and thermal conductivities. Thus by adding graphene nanoplatelets to epoxy resins, the overall mechanical, electrical and thermal properties of the nanocomposite can be improved. This leads to the formation of multifunctional composites, which means that these composites can be used as components that require good mechanical properties and can serve as electrically or thermally conductive components, which can lead to weight savings.

However, this depends three key factors. These are - dispersion of graphene nanoplatelets in the epoxy resin, interaction of the graphene nanoplatelets with the epoxy resin and orientation of graphene nanoplatelets in the epoxy matrix. Since, graphene nanoplatelets tend to form agglomerates at very low loading, hence it is important to study the dispersion, interaction and orientation of GnPs in epoxy resin to achieve optimum fracture resistance.

In the past, studies have been done on the dispersion, interaction and orientation of various types of nanofillers like CNTs, graphene oxide (GO), etc. in epoxy resin and other types of thermoset resin but not much work is present on studying the effects of dispersion, interaction and orientation of pristine graphene nanoplatelets in epoxy resin which is the key focus of this work.

1.1 Studies on Graphene and Dispersion Techniques

Mechanical properties like tensile modulus and tensile strength have been studied before for composites prepared with pristine graphene nanoplatelets and epoxy resin by Julia A. King *et al.* [1] but dispersion techniques were neither implemented nor studied and also fracture toughness wasn't tested.

Fracture energy of composites prepared using functionalized graphene nanosheets (FGS) and epoxy were studied by Mohammad A. Rafiee *et al.* [2] and they showed that fracture energy of 0.125 wt. % FGS-epoxy samples improved by about 115 % when compared to neat epoxy. The functional group in FGS in an oxide group which means they are not pristine graphene and these are essentially graphene oxide (GO).

Fracture toughness of both graphene nanoplatelets and graphene nanosheets (GNS) have been studied by M. M. Shokrieh *et al.* [3] but they did not study the dispersion techniques. In both cases of graphene nanoplatelets and GNS they saw improvement in fracture toughness values when compared to neat epoxy and they recorded highest fracture

toughness values at 0.5 wt.%.

Fracture toughness of graphene-epoxy nanocomposites has been studied by Mohammad A. Rafiee *et al.* [4] but only at a single graphene nanoplatelets loading of 0.1 wt. % and nothing beyond that. The study doesn't report on what happens if more amount of graphene nanoplatelets are incorporated in the epoxy system which is where the dispersion techniques may play an important factor. But it does show improvement in fracture toughness values over neat epoxy samples, SWCNT-epoxy and MWCNT-epoxy samples at the same nanofiller loading.

Mechanical properties of graphene-epoxy nanocomposites were studied along with fracture toughness by Nikolaos D. Alexopoulos *et al.* [5] and it showed improvements in fracture toughness values at low graphene nanoplatelets loading but was not high enough at higher graphene nanoplatelets loadings because dispersion technique was not studied.

Comparison of fracture toughness values of composites prepared using epoxy and different carbon nanofillers like CNTs and graphene nanoplatelets was reported by C. Kostagiannakopoulou *et al.* [6] but this was also done at low graphene content.

It is important to study the effects of dispersion, interaction and orientation of pristine graphene nanoplatelets in epoxy matrix because of the multifunctional properties that pristine graphene nanoplatelets possess and GO does not. GO is not a good conductor of electricity but on the other hand GnPs are good conductors of electricity which is important for certain applications where multifunctionality of a composite is required. Graphene nanoplatelets being good conductors of electricity will also play an important factor in controlling the orientation of graphene nanoplatelets in the epoxy matrix. All this means that it is very important to study the above mentioned effects of graphene nanoplatelets in epoxy resin. After doing a background literature survey of similar work done on GO in

epoxy resin, the knowledge can be used to come up with solutions for dispersing graphene nanoplatelets in epoxy resin. Dispersion of can be achieved by different ways like use of mechanical mixing techniques like ultrasonication, ball milling, etc. and with the help of solvents or surfactants which help in keeping the nanofillers separated from each other as shown in other studies with CNTs or graphene nanoplatelets or GO.

For dispersing nanofillers like graphene nanoplatelets or CNTs in the epoxy matrix, Peng-Cheng Ma *et al.* [15] stated that ultrasonication is one of the best ways to disperse nanoparticles in any medium in terms of ease of use, cost, availability and effectivity. This is because when ultrasonic waves pass through these nanoparticles, it separates the nanoparticles and breaks up the agglomerates. This helps in better distribution of the nanofillers in the bulk matrix.

Ultrasonication was used by Qian *et al.* [26] as the only mechanical mixing method for dispersing CNTs in polystyrene without damaging any of the key ingredients while achieving optimum dispersion and improving tensile strength and elastic modulus.

Among other things, sonication of nanofillers in to the matrix and sonication durations are also very important in order to achieve a good dispersion. There are reasons behind choosing particular sonication durations and also why sonication was done in the first place.

Sonication duration is important as Ghaleb *et al.* [31] talks about how sonication times are crucial and after a point doing sonication for prolonged durations is harmful instead of beneficial. They stated that samples prepared with 20 minutes of sonication time showed higher higher tensile strength and modulus when compared to samples prepared with 10 and 30 minutes of sonication times. This is because graphene nanoplatelets start deforming after prolonged sonication times and lower sonication times is simply isn't long enough or good enough of a time span for proper dispersion.

CNTs are easily damaged under high energy and stress and KL *et al.* [32] reported on the damage and defects found on CNT surfaces after prolonged sonication durations. This completely destroys the purpose of using ultrasonication and instead of achieving composites with superior properties the samples are left with damaged CNTs which are of no use.

Ultrasonication can also cause other effects as Mukhopadhyay *et al.* [33] talked about how CNTs or other carbon nanofillers like graphene are completely destroyed and turn into amorphous carbon when sonicated for too long of a time duration at a stretch.

All these must be kept in mind while using ultrasonication as a mechanical mixing technique because ultrasonication can help in achieving good dispersion of nanofillers in the epoxy matrix but can also damage the nanofillers and thereby destroying the composite as a whole if the ultrasonication durations are not kept in check.

Ball milling is used for dispersing graphene nanoplatelets in polymer matrix as discussed by Guo *et al.*. The high shear stress among the balls in the ball milling chamber breaks the van der Waals interactions between the graphene nanoplatelets layers and thereby preventing the graphene nanoplatelets from sticking together. The authors reported on the improvement in thermal conductivity of the composites as a result of improved dispersion of graphene nanoplatelets in the epoxy due to ball milling.

Ball milling has also been used as a mechanical mixing process as YB *et al.* [34] discussed the effects of ball milling of nanofillers especially CNTs before using them to prepare composites. Ball milling is a high high energy grinding process which helps in production of even fine powdered nanofillers than they already are and it also increases the surface area.

Another mechanical mixing technique used for dispersing nanofillers in epoxy is high speed stirring as Sandler *et al.* [27] used it for dispersing CNTs in epoxy.

All this background information has been utilized in processing samples for the experi-

ments in this study.

Use of solvents and surfactants are important for dispersing graphene in any media or matrix as discussed by Yang *et al.* [10] and they list the strong interaction between the solvent and surfactant molecules and graphene as the key to dispersion. They also talked about surface modified graphene nanoplatelets which when used in preparing nanocomposites showed increase in flexural modulus, flexural strength, impact strength, etc.

Surfactants are adsorbed on to the graphene surface and this prevents re-agglomeration or aggregation of graphene sheets which in turn helps in better dispersion as Jie Yang *et al.* [14] reported on the use of surfactants for dispersion of graphene. They showed that graphene nanosheets are better exfoliated when surfactants are used along with ultrasonication.

For dispersing CNTs in epoxy, Yan Geng *et al.* [16] discussed about use of a particular surfactant, Triton X-100 in order to disperse CNTs for manufacturing nanocomposites. They showed that mechanical properties like Flexural strength, Flexural modulus, Impact strength and electrical conductivity of the nanocomposites improved with increased amount of CNTs used in preparing those.

A study comparing various surfactants was done by Rastogi *et al.* [22] and they used 4 different surfactants Triton X-100, Tween 20, Tween 80 and SDS for dispersion of CNTs. They concluded that Triton X-100 has the highest dispersing power among the four when UV-vis spectra, percent extractability vs concentration and TEM images of various surfactants are compared. They also stated that surfactant should be present in the medium enough to coat the nanofillers but not in excess amount. Excessive amount of surfactant in the medium can inhibit nanofiller dispersion too.

The working mechanism of surfactants was explained by Tkalya *et al.* [23] and they re-

ported on the use of surfactants for dispersing CNTs and graphene for preparing nanocomposites. They used ultrasonication for dispersing the nanofillers in the surfactants. The ionic surfactants used by them in this study are SDBS, SDS, LDS, TTAB and SC. The non-ionic surfactants used are Triton X-100, Tween-80, Tween-60 and Tween-20. The reason behind choosing ultrasonication as a preferred mixing method because the ultrasonic pulses open up the nanofiller agglomerates and then the individual fillers become a site for surfactant adsorbtion. They termed it as an "unzipping" way of separating nanofillers and using the surfactant molecules as way to keep them separated.

Effects of surfactants on the properties of the final composite product was mentioned by Geng *et al.* [24] and they used Triton X-100 for dispersing CNTs in epoxy and studied the properties and showed improvements in storage modulus, flexural strength, flexural modulus, electrical conductivity, etc.

Thermal and mechanical properties of CNT-epoxy composites were improved by Gong *et al.* [29] who used a non-ionic surfactant, polyoxyethylene-8-lauryl for dispersing CNTs in epoxy. They found strong interactions between the carbon of CNTs and the hydrophobic ends of the surfactant and this is a result of van der Waals force and also between the epoxy and the hydrophilic end of the surfactant and that is a result of hydrogen bonding.

Importance of quality of dispersion was shown by Dong *et al.* [19] as they discussed about the use of Triton X-100 for dispersing carbon nanofibers in epoxy resin and also how well it is dispersed. They used different characterization techniques like FTIR, NMR, etc. to judge the quality of dispersion.

GO can be dispersed using surfactants as Texter *et al.* [17] talked about improvements in tensile strength and Young's modulus of graphene oxide nanocomposites after they performed surface modifications of the nanofiller materials and did modification of dis-

persion techniques before adding it to epoxy. They prepared poly(vinyl imidazole) grafted on graphene oxide and then dispersed it in epoxy.

Not only in case of GO or CNTs but also in graphene nanoplatelets researchers have shown that surface modification and dispersion of nanofillers are very important criteria while preparing composites. Chemicals are used for surface modification while surfactants and solvents are used for dispersion. One can be used with or without the other.

Graphene can be dispersed using a wide variety of surfactants and it really depends on what are the intended applications of the prepared samples. Smith *et al.* [21] talks about the importance of using surfactants for dispersion of graphene. They discuss about various ionic surfactants like SDS, SDBS, LDS, CTAB, TTAB, SC, DOC and TDOC and non-ionic surfactants like IGEPAL CO-890, Triton X-100, Tween 20 and Tween 80 which are used or can be used for dispersing graphene. They reported on the level of sedimentation after 7 days, concentration of surfactant, dispersed flake size, UV-vis spectroscopy, degree of exfoliation among others.

Mechanical properties like strength and modulus of composites can be improved by use of surfactants as Ma *et al.* [18] reported on the use of J2000 (polyoxypropylenediamine, Huntsman) a surfactant to disperse graphene nanoplatelets in epoxy and they showed improvements in Young's modulus and tensile strength.

Solvents can also act as a good dispersing agent as the solvent molecules go between the layers of nanofillers and it keeps these nanofillers separated with the help of hydrophobic ends. Iso-propyl alcohol is a very useful solvent and Yamamoto *et al.* [30] dispersed CNTs in first before incorporating them in an epoxy matrix and they talked about how it improved the properties of the composites.

Stronger affinity between the solvent molecules and the graphene particles play an im-

portant role and it prevents the reagglomeration of graphene nanoplatelets due to high energy repulsive barrier as mentioned by Yang *et al.*. Stable solvent layers are present in between graphene particles and thus it keeps them separated and creates a better distribution of GnPs in the matrix.

Functionalization of graphene nanoplatelets are important as shown by Naebe *et al.* [7] and they reported that by performing covalent functionalization on graphene via Bingel reaction, the graphene nanoplatelets were uniformly dispersed in the epoxy resin and the functionalization of graphene also led to very strong interfacial interactions between the epoxy and the graphene nanoplatelets. Their claims were supported by showing 1.22 times increase in flexural strength and 1.18 times increase in storage modulus of the nanocomposite.

Importance of the interaction between the nanofillers and the matrix is discussed by Li *et al.* [8] and to demonstrate it, they have performed surface treatment of graphene by subjecting it to UV/ozone. XPS analysis showed increase in the amount of different functional groups such as hydroxyl, ether and carboxyl groups on the surface on the graphene nanoplatelets. The increasing trend in the different functional groups was very prominent with increase in UV/ozone treatment time. They also showed that the increase in flexural modulus and flexural strength values has a direct relation with the duration of UV/ozone treatment.

Interaction between the nanofillers and the matrix is also improved by Rich *et al.* [9] who used UV treatment to modify the surface of nanofillers used in composite preparation and showed improvements in tensile strength, shear strength, etc. UV treatment of CNTs or graphene nanoplatelets leads to formation of more hydroxyl and carboxyl functional groups on the surface of the particles and this helps in improved tensile strength and interfacial

shear strength.

UV/ozone treatment improves flexural strength of the nanocomposite when compared to its flexural modulus as shown by Li *et al.* [11] who used Tandon-Weng equation to model the bulk modulus and the Reuss 'rule-of-mixtures' equation to model the Young's modulus of the composite based on material properties of the matrix and the filler and demonstrated that their theoretical modeling predictions were close to the actual results and the variations in the results were in range. This was done to validate the changes in modulus values of the composite before and after UV/ozone treatment and to explain the effects of debonding in untreated graphene-epoxy nanocomposite and enhanced interfacial adhesion in UV/ozone treated graphene-epoxy nanocomposite.

Improved dispersion of CNTs in epoxy was demonstrated by Sham *et al.* [12] and they reported on the effects of UV/ozone and solution treatment on surface functionalization of carbon nanotubes. The formation of more carboxyl and amide groups is helpful and desired because these functional groups react with the functional groups present in epoxy and form strong chemical bonds. The treatments also change the hydrophobic nature of CNTs to hydrophilic and thus the functionalized CNTs lead to better dispersion of CNTs in epoxy and also increase the interaction between CNTs and epoxy.

Chemical functionalization of nanofilers is important for improving the interaction between the nanofillers and the epoxy. This is because the functionalized nanofillers will then interact with the epoxy matrix and form bonds and thereby improving the linkage of the nanofillers to the epoxy as a whole which results in enhanced mechanical properties as pointed out by reserachers. Different types of organic chemicals can be used for functionalization of CNTs, GO, etc. like different types of silanes, poly(vinylidene fluoride) (PVF), molecules with amino or hydroxyl groups, etc. The functional groups of these chemicals are

important because these are the ones that interact with both the nanofillers and the epoxy matrix and helps in linking one to the other and maintaining the strong bond.

Chemical functionalization improves the interfacial bond between the nanofiller and the matrix and thus improving mechanical properties like tensile strength in turn as demonstrated by Xie *et al.* [28] who used chemical functionalization by coating CNTs with poly(vinylidene fluoride) and then melt-blended with poly(methyl methacrylate).

Silanes are useful for chemical functionalization of nanofillers like GO and this was shown as Wan *et al.* [13] studied the mechanical properties of graphene oxide epoxy composites when the graphene oxide is functionalized using 3-glycidoxy-propyl-trimethoxy silane (GPTMS). They found a correlation between functionalization of GO and improvement in mechanical properties such as storage modulus, flexural modulus, etc. They inferred that GPTMS functionalized GO showed improved dispersion and interaction with the epoxy matrix and thus led to better mechanical properties.

Another type of silane was used by Li *et al.* [20] who functionalized graphene oxide (GO) using (3-Aminopropyl) trimethoxysilane (APTMS). They studied the reaction between the amino groups of APTMS and the epoxy group and they observed improvement in compressive failure strengths by about 20%.

Other organic chemicals containing amino, alkyl and hydroxyl groups was also used in other cases such as Stevens *et al.* [35] reported on the chemical functionalization of CNTs by adding these chemicals and thereby modifying the CNTs and then using it for preparing composites.

Some other research groups studied different types of chemicals for functionalization and discussed their effects on the dispersion of graphene nanoplatelets in the epoxy matrix like, Wei *et al.* [36] talked about the benefits of chemical functionalization of graphene and that

improved dispersion through it will prevent re-agglomeration of graphene nanoplatelets. Similar work was also done by Worsley *et al.* [37] and they concluded that chemical functionalization of graphene also improves the interaction of graphene with the organic polymer matrices which in turn helps in better dispersion.

Graphene nanoplatelets have also been functionalized using boron nitride nanotubes (BNNTs) by Nadiim Domun *et al.* [38] and used as a hybrid filler material in epoxy and then the fracture toughness values were measured which showed improvements over neat epoxy.

Orientation of graphene nanoplatelets in the epoxy matrix is also important for providing strong barrier against crack propagation while fracture toughness is being tested and this can be done by aligning the graphene nanoplatelets in the epoxy matrix while it is being cured in the mold during the sample preparation process. Such work has been done by Shuying Wu *et al.* [39] and they demonstrated improvement in fracture toughness just by aligning the GnPs in the epoxy matrix in the presence of external electric fields.

1.2 Objective

All these papers make it very clear that graphene nanoplatelets acts as a very good nanofiller material for improving mechanical properties of epoxy nanocomposites and shows better results when compared to other nanofiller and bulk material combinations. This is due to the unique properties and surface characteristics of graphene nanoplatelets and its combination with epoxy resin which makes for better composites with improved mechanical, thermal and electrical properties when compared to neat epoxy or other nanocomposites.

Although a lot of work has been done in recent years with CNTs, GO, graphene nanoplatelets and epoxy, to my knowledge not substantial work has been done regarding the effects of mechanical dispersion techniques, surface treatments and coupling agents on the

fracture toughness of pristine graphene-epoxy nanocomposites. Fracture toughness is important because it is a good way to measure how much load or energy can a sample material withstand before failing. It gives an idea about the load bearing capacity of the material. Depending on whether the sample fails easily at lower loads or can withstand higher loads, decisions can be made where, how and when to use certain composites. It is also important to find out how much amount of graphene nanoplatelets is effective in improving this property of the composite. Researchers have studied the fracture toughness of graphene-epoxy nanocomposites but not while incorporating the dispersion techniques. Those who have looked into the dispersion techniques have not investigated its effects on fracture toughness. This is important because it is not known how ball milling or ultrasonication or surfactants or silanes or a combination of all these effect the fracture toughness of graphene-epoxy nanocomposites. This has not been done before. A combination of such different studies have been done using other nanofillers such as CNTs, etc. but not involving graphene nanoplatelets. Researchers have studied graphene oxide (GO) and reduced graphene oxide (rGO) but not with pristine graphene nanoplatelets. This is what makes this study unique and interesting. It is also unique because the graphene nanoplatelets used in this study is pristine graphene nanoplatelets or 99% graphene nanoplatelets. This is one of the purest form of graphene nanoplatelets available for use in the market and unlike in other studies this type of graphene nanoplatelets is devoid of impurities and defects. Pristine graphene has excellent properties by itself and it has the potential to be the next big nanofiller material. But researchers have struggled with dispersing pristine graphene in epoxy resin matrix and not many studies have been conducted on it. According to my knowledge no one has studied about improved dispersion techniques of these pristine graphene nanoplatelets in epoxy matrix. That is the motivation behind this study. I have tried to come up with a

dispersion technique for uniform distribution of graphene nanoplatelets in epoxy and something that also prevents re-agglomeration. Whether the dispersion technique is superior or not has been validated by testing and measuring the fracture toughness values of the graphene-epoxy test specimen prepared using the new dispersion techniques and by other characterization techniques like Scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy and Transmission optical microscopy (TOM). It will be very interesting to see how pristine graphene nanoplatelets perform when mechanical dispersion techniques like ball milling and ultrasonication, surfactants like Triton X-100 and silanes like GPTMS and APTMS are used for dispersing it into epoxy resin. This work is an effort to combine the knowledge from all previous works done by researchers on graphene and similar other nanofillers using different types of dispersion techniques and other chemicals while trying showcase its effects on the fracture toughness of the final product i.e., the graphene-epoxy nanocomposites.

The objective of this study is to investigate the dispersion techniques and surface functionalization of graphene nanoplatelets by incorporating it in diglycidyl ether of bisphenol F (DGEBF) epoxy resin and curing it with an aliphatic amine and to improve the fracture toughness of graphene-epoxy nanocomposites. In this study, graphene nanoplatelets were incorporated in epoxy resin at different loadings in order to understand the effect of increasing graphene nanoplatelet loading on neat epoxy. Some graphene nanoplatelets went under modification techniques before being incorporated into epoxy resin and some of those modified graphene nanoplatelets were functionalized using GPTMS and APTMS. Fracture toughness test was performed on the prepared samples for evaluating the mechanical properties. Scanning electron microscopy (SEM) was performed for understanding the crack propagation behavior in the samples during the fracture toughness test. Fourier transform

infrared (FTIR) spectroscopy was performed for assessing the amount of modification of graphene nanoplatelets. Transmission optical microscopy (TOM) was performed for examining the quality of dispersion of graphene nanoplatelets.

Improved dispersion of modified and functionalized graphene nanoplatelets was observed compared to unmodified or poorly dispersed GnPs in epoxy. Ball milling, ultrasonication play important role as mechanical mixing or mechanical dispersion techniques. The fracture toughness values of the graphene-epoxy samples processed suing various techniques were measured and compared against each other and it shows that modification of processing and dispersion techniques plays a significant role in improving the fracture toughness values of graphene-epoxy nanocomposites.

CHAPTER II

EXPERIMENTAL METHODS

The raw materials used for the experiments are -- graphene nanoplatelets, an amine cured DGEBF based epoxy resin, an amine based curing agent, a solvent (isopropyl alcohol), a surfactant (Triton X-100) and two silanes (GPTMS and APTMS). The epoxy resin and the curing agent were purchased from Miller Stephenson (Danbury, CT, US). The epoxy resin used is EPON 862, which is a diglycidyl ether of bisphenol f based resin. A few advantages of this epoxy resin are that it has low viscosity and good chemical resistance and it displays better adhesive, mechanical and electrical properties when paired with suitable curing agents. The curing agent used is EPIKURE 3274 and it is an aliphatic amine based curing agent. The graphene nanoplatelets were purchased from XG Sciences (Lansing, MI, US) and these are 99% pristine graphene nanoplatelets and are of grade M-5. The average thickness of these graphene nanoplatelets is about 6 to 8 nm with particle diameter about 5 microns. The solvent used is isopropyl alcohol and it was purchased from VWR (Radnor, PA, US). The surfactant used is 4-(1,1,3,3-Tetramethylbutyl) phenyl-polyethylene glycol or Triton X-100 and it was purchased from Sigma-Aldrich (St. Louis, MO, US). The two different silanes are 3-glycidoxypropyltrimethoxy silane (GPTMS) and (3-Aminopropyl) trimethoxysilane (APTMS) respectively and these were purchased from Sigma-Aldrich (St. Louis, MO, US).

2.1 Material Preparation

Four different processing techniques were used for preparing the GNP-epoxy nanocomposites. These were based on mechanical dispersion including ultrasonication and ball milling, use of the surfactant and use of the two different types of silanes.

In a typical sample preparation process 150 grams of EPON 862 epoxy resin was used along with 60 grams of EPIKURE 3274 curing agent. The ratio of epoxy resin to curing agent is 100:40 by weight. Graphene nanoplatelets were added to the epoxy in amounts of 0.1, 0.2, 0.5, 1.0 and 2.0 wt.% and the weight ratio is based on the final weight of the epoxy system. So the total weight of the two part epoxy system is always 210 grams because 150 grams of epoxy resin and 60 grams of curing agent is used. Based on that 0.1 wt.% loading equates to 0.21 grams of graphene nanoplatelets, 0.2 wt.% loading equates to 0.42 grams of graphene nanoplatelets, 0.5 wt.% loading equates to 1.05 grams of graphene nanoplatelets, 1.0 wt.% loading equates to 2.1 grams of graphene nanoplatelets and 2.0 wt.% loading equates to 4.2 grams of graphene nanoplatelets. These were the graphene nanoplatelets amounts added to the epoxy system by weight for preparing all the different types of samples.

Table 2 lists the sample preparation techniques of all the different types of samples prepared and tested in this experiment. Graphene nanoplatelets are denoted as GnPs. Ball milling as BM. Ultrasonication as US. Triton X-100 as TX-100.

2.2 Unmodified Material Preparation Technique

For preparation of unmodified graphene-epoxy samples, the graphene nanoplatelets did not undergo any modification. As-received graphene nanoplatelets were used for preparation of graphene-epoxy nanocomposites. In this method, graphene-epoxy nanocomposites were

Table 1: Sample Preparation Technique

Process	Description
Neat	No GnPs. Only epoxy and curing agent
Unmodified	Unmodified as received GnPs + epoxy + curing agent
Ball Milled	BM GnPs + epoxy + curing agent
Triton X-100	TX-100 + BM GnPs + epoxy + curing agent
GPTMS	GPTMS + BM GnPs + TX-100 + epoxy + curing agent
APTMS	APTMS + BM GnPs + TX-100 + epoxy + curing agent

prepared with as received graphene nanoplatelets, epoxy and curing agent. Also, in this technique no other chemicals were used. At first, 150 grams of liquid epoxy was drawn into a beaker and it was heated with a magnetic bead in it on a hot plate at 70 degree Celsius and 200 rpm. After 30 minutes of heating the epoxy, when the viscosity of the epoxy was reduced, GnPs were added to it. The graphene nanoplatelets loadings used for the experiments are - 0.1, 0.2, 0.5, 1.0 and 2.0 weight percentages of the total weight of the epoxy and curing agent used for preparing the samples. According to Miller-Stephenson, the epoxy to curing agent ratio is 100/40 by weight. So for 150 grams of epoxy, 60 grams of curing agent had to be used and the total weight of epoxy and curing agent of the final product is 210 grams. From this, it was calculated how much graphene nanoplatelets had to be added for different graphene nanoplatelets loadings. After, the graphene nanoplatelets were added to the liquid epoxy in the beaker, the mixture was heated and mixed for 24 hours on the hot plate at 70 degree Celsius and 200 rpm for achieving homogenous distribution of graphene nanoplatelets in epoxy. After 24 hours of heating and mixing of graphene nanoplatelets in the liquid epoxy, this process was stopped and the beaker was taken off the hot plate and left to cool down for 30 minutes. Then, the graphene-epoxy mixture was ultrasonicated in an ice bath for 2 cycles of 10 minutes each. The mixture was also allowed to cool for 30 minutes in between cycles. After the second stage of ultrasonication was

over, the mixture was once more allowed to cool for 30 minutes before adding the curing agent. EPIKURE 3274 curing agent was then added to the graphene-epoxy mixture and the mixing process was done manually with a tongue depressor for 15 minutes for achieving a homogenous distribution of graphene nanoplatelets, epoxy and curing agent. After this, the mixture was vacuum degassed for 15 minutes for removal of bubbles from the mixture because while mixing the curing agent to epoxy, air gets entrapped in the system. After vacuum degassing was done, the bubbles come to the surface of the mixture and it was manually and carefully removed from the top surface of the mixture. Then the mixture was poured into a mold made up of aluminum plates. The mixture was left in the mold for 24 hours at room temperature so that the curing process is complete. After 24 hours, the cured sample was taken out of the mold and placed in an oven for post curing. The sample was put in oven for 6 hours at a high temperature of 121 degree Celsius. These post curing parameters were implemented according to Miller-Stephenson guidelines. After post curing was done, sample was taken out of oven and it was ready for various types of characterization techniques and other testings. The samples prepared according to this method are identified as unmodified graphene-epoxy samples.

2.3 Material Preparation by Mechanical Dispersion including Ball Milling

In the first method, measured graphene nanoplatelets were first ball milled for in a Retsch (Dusseldorf, Germany) PM 200 Planetary Ball Mill for 60 minutes at 200 rpm. The ratio of weight of balls used in the ball milling machine to the graphene nanoplatelets is 10:1. Ball milled graphene nanoplatelets were then added to a beaker filled with 100 ml of isopropyl alcohol (IPA). This mixture of graphene nanoplatelets and IPA was then sonicated in 3 steps of 10 minutes each with intervals of 15 minutes in between sonicating periods. Liquid epoxy was heated and mixed on a hot plate for 30 minutes at 70 degree Celsius and 200

rpm before the mixture of IPA and graphene nanoplatelets was added to it. This mixture was continuously heated and mixed for 24 hours at 70 degree Celsius and 200 rpm. After 24 hours of heating and mixing of graphene nanoplatelets in the liquid epoxy, this process was stopped and the beaker was taken off the hot plate and left to cool down for 30 minutes before adding the curing agent. The rest of the process is the same as mentioned in the unmodified material preparation technique. After post curing was done, sample was taken out of oven and it was ready for various types of characterization techniques and other testings.

2.4 Material Preparation by Addition of Surfactant Triton X-100

In the second method, measured graphene nanoplatelets were first ball milled for in a Retsch (Dusseldorf, Germany) PM 200 Planetary Ball Mill for 60 minutes at 200 rpm. Ball milled graphene nanoplatelets were then added to a beaker filled with 100 ml of isopropyl alcohol (IPA) and this time Triton X-100 was added to it. This mixture of graphene nanoplatelets, Triton X-100 and IPA was then sonicated in 3 steps of 10 minutes each with intervals of 15 minutes in between sonicating periods. Liquid epoxy was heated and mixed on a hot plate for 30 minutes at 70 degree Celsius and 200 rpm before the processed graphene nanoplatelets were added to it. This mixture was continuously heated and mixed for 24 hours at 70 degree Celsius and 200 rpm. After 24 hours of heating and mixing of graphene nanoplatelets in the liquid epoxy, this process was stopped and the beaker was taken off the hot plate and left to cool down for 30 minutes. Then, the graphene-epoxy mixture was ultrasonicated in an ice bath for 2 cycles of 10 minutes each. The mixture was also allowed to cool for 30 minutes in between cycles. After the second stage of ultrasonication was over, the mixture was once more allowed to cool for 30 minutes before adding the curing agent. The rest of the process is the same as mentioned in the unmodified material preparation technique.

After post curing was done, sample was taken out of oven and it was ready for various types of characterization techniques and other testings.

2.5 Material Preparation by Addition of Two Different Silanes, GPTMS and APTMS

In the third method, measured graphene nanoplatelets were first ball milled for in a Retsch (Dusseldorf, Germany) PM 200 Planetary Ball Mill for 60 minutes at 200 rpm. Ball milled graphene nanoplatelets were then added to a beaker filled with 100 ml of isopropyl alcohol (IPA) and this time Triton X-100 was added to it. This mixture of graphene nanoplatelets, Triton X-100 and IPA was then sonicated in 3 steps of 10 minutes each with intervals of 15 minutes in between sonicating periods. Measured amount of GPTMS was then added to the mixture and it was left to mix on a hot plate for 24 hours at a temperature of 80 degree Celsius. After that, the mixture was vacuum dried for 24 hours at a temperature of 80 degree Celsius. Liquid epoxy was heated and mixed on a hot plate for 30 minutes at 70 degree Celsius and 200 rpm before the dried GPTMS-f-graphene nanoplatelets were added to it. This mixture was continuously heated and mixed for 24 hours at 70 degree Celsius and 200 rpm. After 24 hours of heating and mixing of graphene nanoplatelets in the liquid epoxy, this process was stopped and the beaker was taken off the hot plate and left to cool down for 30 minutes. Then, the graphene-epoxy mixture was ultrasonicated in an ice bath for 2 cycles of 10 minutes each. The mixture was also allowed to cool for 30 minutes in between cycles. After the second stage of ultrasonication was over, the mixture was once more allowed to cool for 30 minutes before adding the curing agent. The rest of the process is the same as mentioned in the unmodified material preparation technique. After post curing was done, sample was taken out of oven and it was ready for various types of characterization techniques and other testings.

The fourth method simply consisted of third method repeated step by step using APTMS instead of GPTMS for preparing the APTMS functionalized graphene-epoxy samples.

A neat epoxy sample was also fabricated so that we can compare the different properties of epoxy composites with and without graphene nanoplatelets loading. For the neat epoxy sample, liquid epoxy was heated on a hot plate for 24 hours at 70 degree Celsius and 200 rpm and the rest of the process is same as that of the first method. The only obvious difference being that, no amount of graphene nanoplatelets were added in this case whatsoever.

Once the composite plates were cast, these were cut and machined using a diamond precision saw according to test standards for performing characterization and testing of the prepared specimen.

2.6 Characterization and Testing

Transmission optical microscopy (TOM) was carried out on freshly dispersed samples to observe the dispersion. A droplet of the different types of samples dispersed using different techniques were taken on separate glass slides and then those were examined in an optical microscope (Nikon, Tokyo, Japan)

Fourier transform infrared (FTIR) spectroscopy was performed on as received graphene nanoplatelets, dispersed graphene nanoplatelets and functionalized graphene nanoplatelets in order to understand the interactions between the graphene nanoplatelets and the epoxy. As received graphene nanoplatelets are already in powdered form but in other cases the samples were powdered using a laboratory grinder. The different test specimen were added to potassium bromide (KBr) in the ratio of 1:99 by weight. The potassium bromide (KBr) powder acts as the background. The samples were tested in an FTIR spectrometer (Nicolet iS10, Waltham, MA) and subjected to 64 scans at a resolution of 4.0 cm-1. The spectrum was collected at room temperature between 4000 and 500 cm-1.

Single edge notch bending (SENB) test was performed for calculating and measuring the mechanical properties such as fracture toughness values of the unmodified and modified graphene-epoxy nanocomposites and neat epoxy. This test was performed as per ASTM D5045 standard testing guidelines. The prepared neat, unmodified and modified graphene-epoxy samples were cut according to the standard guidelines. The test specimen dimensions were 54 mm $\times$ 12.7 mm $\times$ 6.3 mm (length $\times$ width $\times$ thickness). A notch was made on each test specimen and then a sharp crack was initiated by tapping a fresh razor with a hammer on the notched specimen. Only those specimen were tested which had an a/W ratio between 0.45 and 0.55 as per ASTM D5045 where a and W are the crack length and specimen width respectively. The crack length ranged between 5.7 and 6.9 mm. The cracked single edge notched specimen were tested on an universal testing machine (Instron, Norwood, MA, US). The tests were performed in a displacement controlled mode with a fixed cross-head speed of 10 mm/min. The load and crosshead displacement were recorded during testing. The fracture toughness of the test specimen were calculated in terms of critical stress intensity factor K_{IC} which was calculated using. For each type of sample, 5 specimens were tested and the test results were noted and recorded. After testing was complete, all specimens were carefully stored so that the fractured surface is not tampered with.

The morphology of the fractured surface of the test specimen was determined by scanning electron microscopy (SEM). SEM was performed using Hitachi S-4800 SEM (Hitachi, Tarrytown, NY, US). Before performing SEM, the fractured surface of different specimen were sputtered with gold nanoparticles to enhance the electrical conductivity of the specimen and to minimize charge accumulation during imaging.

CHAPTER III

RESULTS AND DISCUSSION

The fracture toughness K_{IC} values of the different graphene-epoxy test specimen were calculated using the data obtained from the SENB test as per ASTM D5045. It was then plotted for both unmodified and modified types of graphene-epoxy nanocomposite samples at different graphene nanoplatelets loadings. The fracture toughness values showed significant increase with increase in graphene nanoplatelets loading in case of modified samples over the unmodified samples till a certain point but after that the it became steady. This phenomenon happened for both unmodified and modified samples. Overall the fracture toughness values for the modified graphene-epoxy samples were higher than that of the unmodified samples at all graphene nanoplatelets loadings. This can be attributed to the better dispersion of graphene nanoplatelets in the liquid epoxy achieved through the modification processes. Ball milling of graphene nanoplatelets and addition of surfactants and silanes must have led to better exfoliation of graphene nanoplatelets which resulted in a uniform distribution of graphene nanoplatelets in the liquid epoxy matrix and formation of strong bonding and cross linking between graphene nanoplatelets and epoxy. At higher graphene nanoplatelets loadings, the change in fracture toughness values in case of modified samples over the unmodified samples was pronounced. Also, for both unmodified and unmodified samples, the fracture toughness values did show a lot of improvement at higher loadings.

3.1 Fracture Toughness

The steady increase in fracture toughness values was witnessed for 0.1 wt.%, 0.2 wt.%, 0.5 wt.%, 1.0 wt.% and 2.0 wt.% graphene nanoplatelets loadings of unmodified and modified GnP-epoxy samples. The fracture toughness values for modified samples were higher than that of the unmodified samples for each of these particular graphene nanoplatelets loadings.

Table 2 lists the fracture toughness values with standard deviation of all the different types of samples prepared and tested in this experiment.

Table 2: Fracture Toughness Data

GnP Loading	Unmodified	Ball Milled	Triton X-100	GPTMS	APTMS
wt. %	MPa.m1/2	MPa.m1/2	MPa.m1/2	MPa.m1/2	MPa.m1/2
0	0.9±0.2	0.9±0.2	0.9±0.2	0.9±0.2	0.9±0.2
0.1	0.9±0.3	1.2±0.3	1.7±0.6	1.2±0.2	1.3±0.4
0.2	1.2±0.3	1.3±0.2	1.8±0.1	1.3±0.2	1.6±0.3
0.5	1.4±0.3	1.6±0.4	1.9±0.2	1.9±0.3	2.0±0.4
1.0	1.3±0.4	1.4±0.1	1.9±0.5	2.0±0.1	2.2±0.2
2.0	1.5±0.1	1.5±0.2	2.1±0.3	2.0±0.1	2.1±0.4

When comparing unmodified graphene-epoxy samples and graphene-epoxy samples modified using the mechanical dispersion technique or ball milling as a way of dispersing, some changes in fracture toughness can be seen. In case of 0.1 wt.% graphene-epoxy nanocomposites, the fracture toughness (K_{IC}) value increased by 24.46%. In case of 0.2 wt.% graphene-epoxy nanocomposites, the fracture toughness value increased by 14.53%. In case of 0.5 wt.% graphene-epoxy nanocomposites, the fracture toughness value increased by 9.92%. In case of 1.0 wt.% graphene-epoxy nanocomposites, the fracture toughness value increased by 10.93%. In case of 2.0 wt.% graphene-epoxy nanocomposites, the Fracture Toughness value decreased by 1.99% and ±1

When comparing unmodified graphene-epoxy samples and graphene-epoxy samples modified using the surfactant Triton X-100, some improvements in fracture toughness can be

seen. In case of 0.1 wt.% graphene-epoxy nanocomposites, the fracture toughness value increased by 84.04%. In case of 0.2 wt.% graphene-epoxy nanocomposites, the fracture toughness value increased by 90.59%. In case of 0.5 wt.% graphene-epoxy nanocomposites, the fracture toughness value increased by 34.75%. In case of 1.0 wt.% graphene-epoxy nanocomposites, the fracture toughness value increased by 51.56%. In case of 2.0 wt.% graphene-epoxy nanocomposites, the fracture toughness value increased by 38.41%.

When comparing unmodified graphene-epoxy samples and graphene-epoxy samples modified using graphene nanoplatelets functionalized with GPTMS, some improvements in fracture toughness can be seen. In case of 0.1 wt.% graphene-epoxy nanocomposites, the fracture toughness value increased by 31.91%. In case of 0.2 wt.% graphene-epoxy nanocomposites, the fracture toughness value increased by 13.67%. In case of 0.5 wt.% graphene-epoxy nanocomposites, the fracture toughness value increased by 32.62%. In case of 1.0 wt.% graphene-epoxy nanocomposites, the fracture toughness value increased by 58.59%. In case of 2.0 wt.% graphene-epoxy nanocomposites, the fracture toughness value increased by 32.45%.

When comparing unmodified graphene-epoxy samples and graphene-epoxy samples modified using graphene nanoplatelets functionalized with APTMS, some improvements in fracture toughness can be seen. In case of 0.1 wt.% graphene-epoxy nanocomposites, the fracture toughness value increased by 39.36%. In case of 0.2 wt.% graphene-epoxy nanocomposites, the fracture toughness value increased by 35.04%. In case of 0.5 wt.% graphene-epoxy nanocomposites, the fracture toughness value increased by 38.29%. In case of 1.0 wt.% graphene-epoxy nanocomposites, the fracture toughness value increased by 70.31%. In case of 2.0 wt.% graphene-epoxy nanocomposites, the fracture toughness value increased by 35.76%.

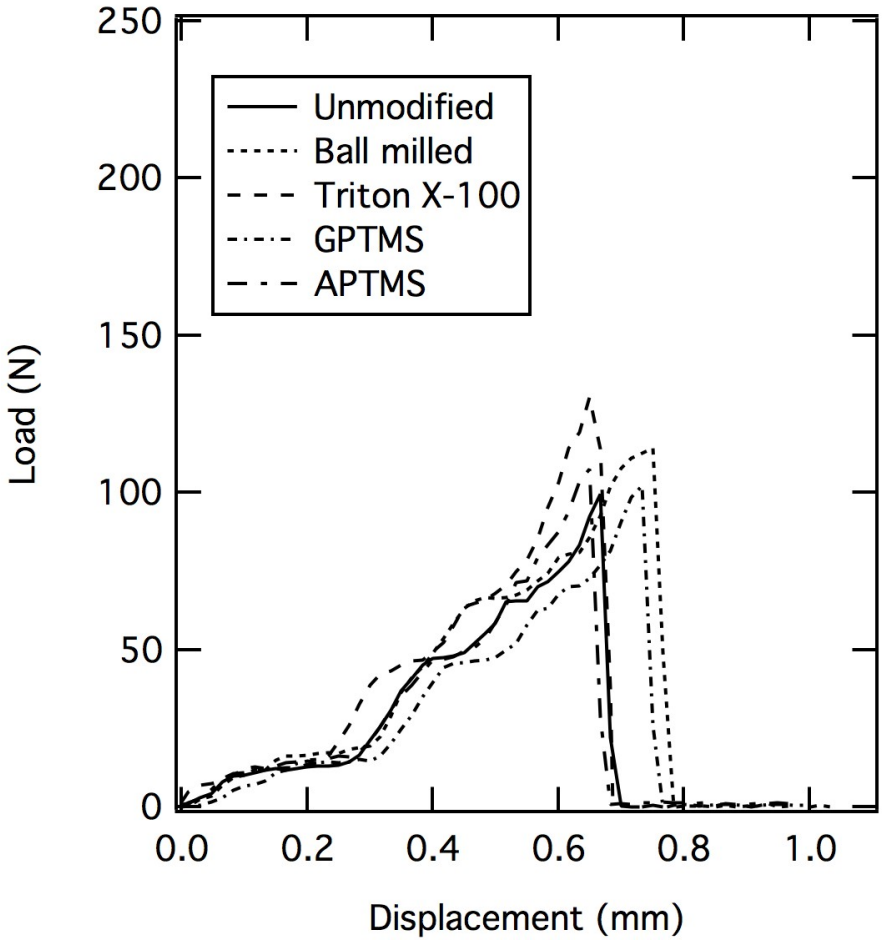


Figure 1: Load Displacement graph of 0.2 wt.% graphene-epoxy nanocomposites

Figure 1 shows the load displacement curves of 0.2 wt.% graphene-epoxy nanocomposites with similar crack lengths. It can be seen that the graphene-epoxy samples prepared using the dispersion technique (including ball milling and TX-100) and the samples prepared using the 2 different types of silanes (GPTMS and APTMS) have the highest loads among the other curves. Although these samples have the highest loads but still the peak loads of all the different types of samples are very close to each other and thus it shows that the amount of graphene nanoplatelets in the samples is simply not high enough at 0.2 wt.% to show significance in the difference of processing techniques.

Figure 2 shows the load displacement curves of 1.0 wt.% graphene-epoxy nanocomposites with similar crack lengths. It can be seen that the graphene-epoxy samples prepared using the dispersion technique (including ball milling and TX-100) and the samples prepared using the 2 different types of silanes (GPTMS and APTMS) have the highest loads among the other curves. Although the unmodified load curve has high load it doesn't have high displacements which means that it cracks easily and is brittle.

Figure 3 shows the complete set of Fracture toughness data for graphene-epoxy samples processed using all the different techniques and for every graphene nanoplatelets loading used for making those samples.

Fracture toughness values of modified and dispersed graphene-epoxy samples have shown clearly improvements when compared to unmodified graphene-epoxy samples. Especially at lower graphene nanoplatelets loadings and till 1 wt.% the improvement in Fracture Toughness values is quite significant. But as we keep increasing the graphene nanoplatelets loading in the epoxy after 1 wt.% the Fracture Toughness values don't show much improvement over the previous graphene nanoplatelets loading and become steady instead of improving. The average fracture toughness values of all 0.2 wt.% graphene-epoxy samples is 1.5 MPa.m$^{1/2}$

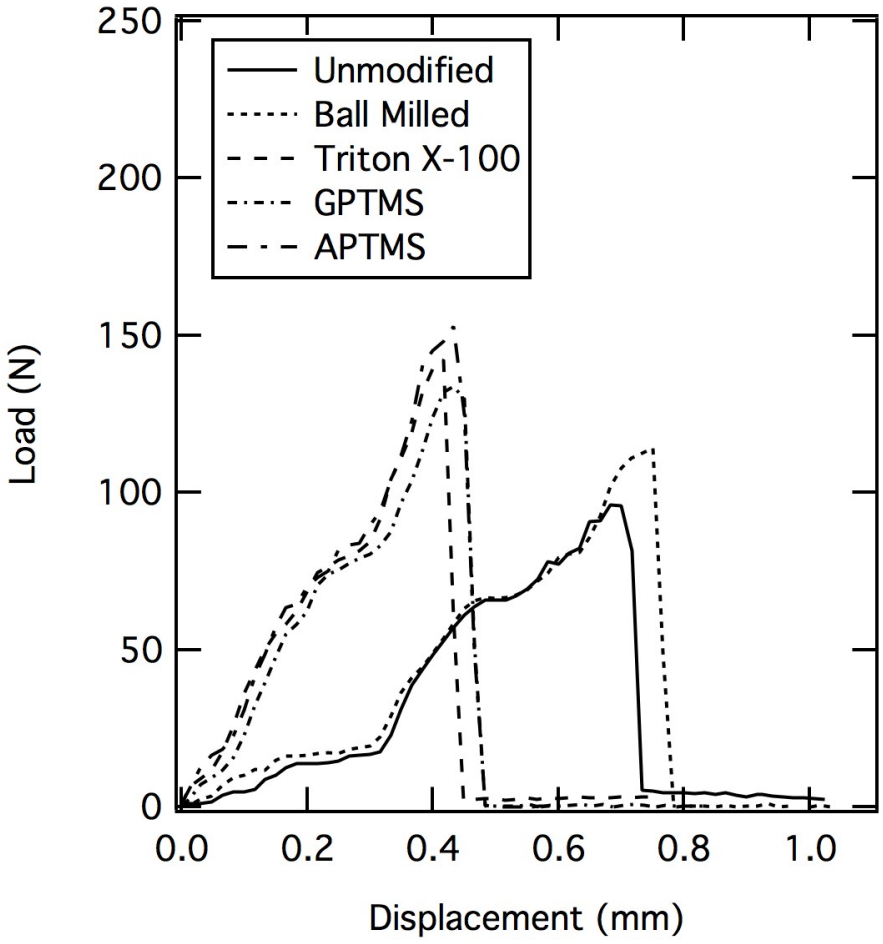


Figure 2: Load Displacement graph of 1.0 wt.% graphene-epoxy nanocomposites

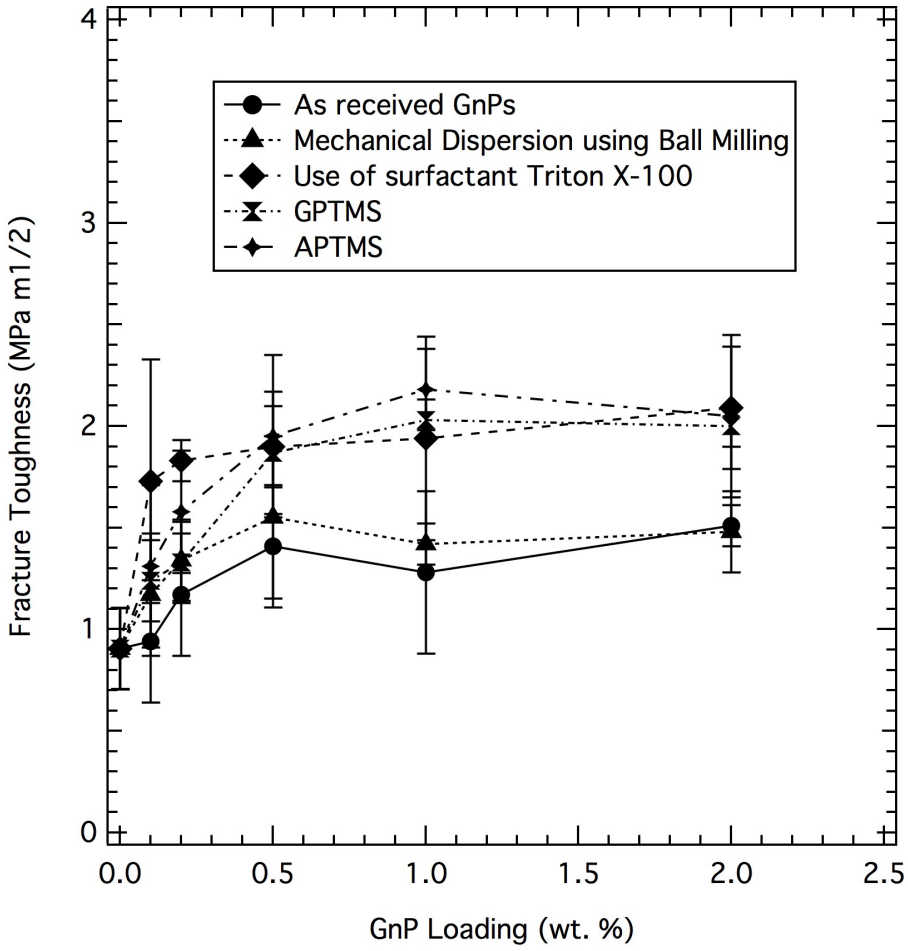


Figure 3: Fracture toughness of neat and graphene-epoxy nanocomposites

and that is an improvement of over 60% when compared to neat epoxy samples. In case of 1.0 wt.% graphene-epoxy samples the average fracture toughness value is 1.8 MPa.$m^{1/2}$ and that is an improvement of over 95% when compared to neat epoxy samples.

The same phenomenon can be observed for samples processed using APTMS and GPTMS. They both show negligible to no improvement over modified graphene-epoxy samples and and don't show any improvement at all at higher graphene nanoplatelets loadings. This is because of two reasons. First of all these are mostly pristine and 99% pure graphene nanoplatelets and these don't have many active on their surface and that makes it difficult to functionalize with chemicals like silanes because the chemicals need active sites for proper functionalization. It helps if there are functional groups like hydroxyl groups and other active groups present on the surface of the graphene nanoplatelets. These help in forming strong chemical bonds between the graphene nanoplatelets and the silanes. In this study, due to the graphene nanoplatelets being 99% pristine there aren't too many of those functional groups present on the surface but there are still a few of those and that helps in forming very few bonds. Also the second point is that a certain amount of graphene nanoplatelets is enough for providing optimum fracture toughness values. Too low or too high graphene nanoplatelets content in the epoxy matrix will eventually lead to poorly dispersed samples with sites rich in graphene nanoplatelets or sites devoid of graphene nanoplatelets in the epoxy matrix which will eventually lead to the failure of the composite structure due to being unable to prevent cracks from propagating through.

Typical load displacement data from fracture toughness experiments is shown in for two different cases of graphene nanoplatelets loading in the matrix. All the graphene-epoxy samples used for demonstrating the load-displacement plots have same crack length. They all showed similar behavior for the load-displacement graphs.They are all wavy in nature.

They all have sharp load decrease at point of failure. They all have similar peak loads for 0.2 wt.% graphene-epoxy samples. They have similar peak loads for 1.0 wt.% graphene-epoxy samples as well but only for certain cases.

The wavy nature of the load displacement graphs of all graphene-epoxy composite samples and especially the modified samples denote something known as pre-crack growth. The load-displacement line is not a straight line because of the following reasons. When the crack tries to propagate through the sample, the graphene nanoplatelets try to prevent and stop the cracks from growing. The load component of the growth spikes up after the penetrating crack hits every graphene nanoplatelets on its way through the sample while the sample is on its way to failure. It requires a higher load to break through the graphene nanoplatelets at every point so every tiny peak on that graph denotes an encounter between the growing crack and graphene nanoplatelets. When the crack is successful in breaking through graphene nanoplatelets it goes through a small region low in graphene nanoplatelets and that's what is denoted by the valleys on the load-displacement plots. This series of peaks and valleys keeps going on and is observed throughout the load-displacement curves of all sample until they completely fail. The graphene nanoplatelets fail to prevent the crack from growing and breaking the sample apart only after a critical stress intensity factor is reached. This is the measure of fracture toughness.

This is why it is so important to have as much or as many graphene nanoplatelets as possible in the way of the crack growth plane. These graphene nanoplatelets will act as a strong barrier against the cracks. The more dispersed the graphene nanoplatelets are in the epoxy matrix, the higher the probability of the graphene nanoplatelets being present in the epoxy almost everywhere which means the higher the chances for the cracks to come in contact with these. Simply adding more graphene nanoplatelets to the epoxy won't

help the cause since these graphene nanoplatelets tend to form agglomerates and that will lead to regions in the composites with lumps of graphene nanoplatelets and other regions where there are almost no graphene nanoplatelets. The regions with low or close to none graphene nanoplatelets will not be able to act as a barrier to the crack propagation at all and thus will be unable to sustain high loads and will fail at much lower loads thereby leading to lower fracture toughness values which is not desirable. This is why proper dispersion of graphene nanoplatelets in the epoxy resin matrix is so crucial. Uniformly distributed graphene nanoplatelets in the epoxy resin matrix means there are no sites where graphene nanoplatelets are forming lumps and also no sites where are no graphene nanoplatelets at all. This homogeneous distribution of graphene nanoplatelets mean that graphene nanoplatelets are present everywhere and therefore cracks have to encounter the graphene nanoplatelets almost everywhere in the sample no matter which path they try to take in order to propagate through the sample. There will be no easy way for the cracks to propagate through with facing the graphene nanoplatelets and which in turn will make the crack difficult to break through the sample. And having the graphene nanoplatelets in the crack growth path means that the graphene-epoxy composite system as a whole will have higher load bearing capacities and fail at a much higher load thereby giving rise to higher fracture toughness values which is the aim of this study.

Due to the dispersion techniques being used, the graphene nanoplatelets are better distributed in the epoxy resin. This means that there are more chances of crack paths encountering graphene nanoplatelets when samples are being tested for fracture toughness. The dispersed graphene nanoplatelets are preventing cracks to grow and or propagate through the sample up to a certain load point and only after which it fails. In case of unmodified samples the graphene nanoplatelets are scattered unevenly throughout the epoxy resin

matrix and thus leaving a lot of regions where there are almost no graphene nanoplatelets present and in some regions there are clusters or agglomerates of graphene nanoplatelets. This means that the graphene nanoplatelets void regions provide no barrier to cracks trying to propagate through the material while testing at all. This is the reason why unmodified or neat epoxy samples have lower load bearing capacity. This is mostly true for all graphene nanoplatelets loadings in the epoxy resin or at least that's what is seen in this study. Unmodified samples at higher graphene nanoplatelets loadings are actually worse because more graphene nanoplatelets mean bigger agglomerates formed at certain regions in the samples and thereby leading to bigger and more number of void or empty spaces. This combination of agglomerates and voids lead to critical sites of failure in the samples and thus fracture toughness is not improved even though amount of graphene nanoplatelets are improved in the system. This is why proper and uniform dispersion of graphene nanoplatelets in the epoxy matrix is so important. When the different dispersion techniques are implemented that include mechanical mixing and use of surfactants, it prevents the graphene nanoplatelets from forming clusters.

This could be due to the fact that there is a threshold limit of adding graphene nanoplatelets to the epoxy no matter what processing or dispersion techniques are used. Beyond 1 wt.% graphene nanoplatelets loading there is no more increase in fracture toughness values when compared to lower graphene nanoplatelets loadings and this is possibly the best result that has been produced with the current techniques and materials.

3.2 Scanning Electron Microscopy

The morphology of the fractured surfaces of the test specimen for unmodified, modified and neat epoxy samples was analyzed by Scanning electron microscopy (SEM). From the SEM images, we can clearly see the differences in surface characteristics of neat, unmodified

and modified graphene-epoxy samples. In case of the neat epoxy sample, there are almost no visible crack lines. This is because in the neat epoxy sample, there are no particles which can act as an obstacle to the crack growth or try to prevent it from cracking. This results in a near smooth fractured surface of the test specimen. In case of the unmodified 0.2 wt.% graphene-epoxy sample, the fractured surface is rough but we can see what looks like to be some form of an aggregate of graphene nanoplatelets in the specimen. But in case of the modified 0.2 wt.% graphene-epoxy sample, there are no visible aggregates. Both unmodified and modified samples with 1.0 wt.% graphene nanoplatelets loading, have fracture surfaces that look very rough and have more characteristics than the samples with 0.2 wt.% graphene nanoplatelets loadings. This is due to the fact that more amount of graphene nanoplatelets in the sample means more hindrance to the crack growth and crack propagation is not smooth and hence surface looks rough. This is roughly the same for all graphene nanoplatelets loadings when modified samples are compared to unmodified samples. More amount of graphene nanoplatelets lead to more crack lines and this is a result of extrinsic toughening mechanism provided by the graphene nanoplatelets in the epoxy.

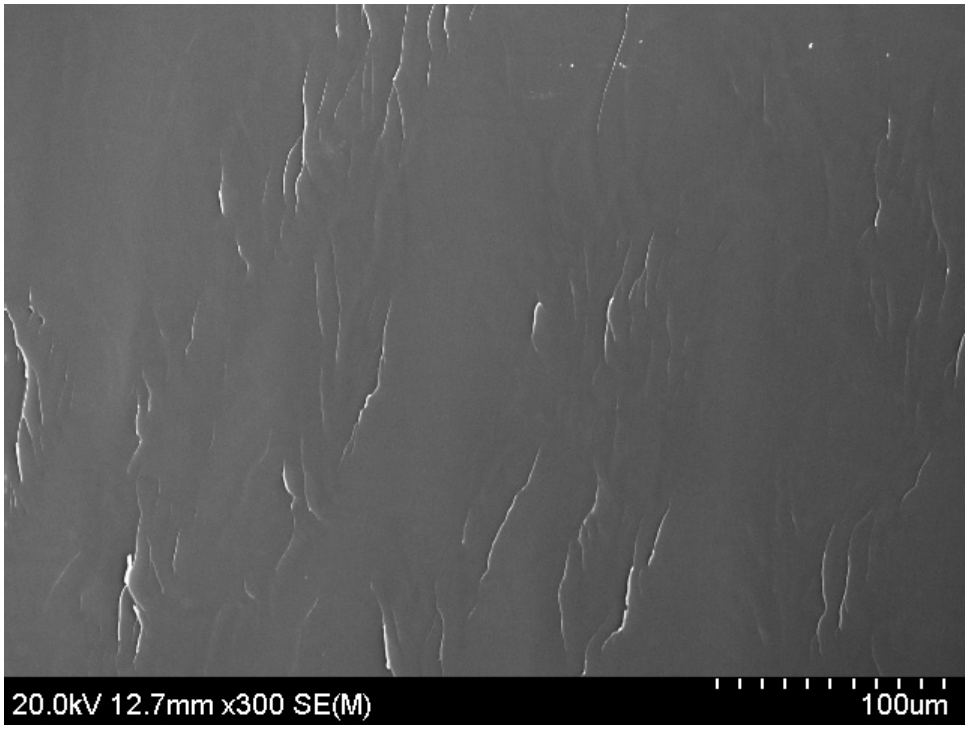


Figure 4: SEM of Neat Epoxy

From the illustrations in figure 5 and 6 SEM images above it can be clearly seen that fractured surface looks more rough and has more characteristics when amount of graphene nanoplatelets are increased in the epoxy resin. Figure 4 shows that neat epoxy resin has very little to no characteristics or crack lines at all. On the other hand, there are a lot more visible characteristics and crack lines in the 0.2 and 1.0 wt.% graphene-epoxy samples.

From figure 7 and figure 8 SEM images it can be inferred that fractured surface looks more rough and has more characteristics when amount of graphene nanoplatelets are increased in the epoxy resin. In this case the graphene nanoplatelets are functionalized using GPTMS. Sample with 0.2 wt.% it has more characteristics than unmodified 0.2 wt.% sample. Similarly, there are a lot more visible characteristics and crack lines in the 0.2 and 1.0 wt. % graphene-epoxy samples. We can see a lot of cracks at higher loadings as well.

From figure 9 and figure 10 SEM images it can be observed that fractured surface looks more rough and has more characteristics when amount of modified graphene nanoplatelets are increased in the epoxy resin. Even at 0.2 wt.% it has more characteristics than unmodified 0.2 wt.% sample. Similarly, there are a lot more visible characteristics and crack lines in the 0.2 and1.0 wt. % graphene nanoplatelets-epoxy samples.

From figure 11 and figure 12 SEM images it is clear that fractured surface looks more rough and has more characteristics when amount of graphene nanoplatelets are increased in the epoxy resin. In this case the graphene nanoplatelets are functionalized using APTMS. This time at 0.2 wt.% it has less characteristics than modified or GPTMS grafted graphene nanoplatelets 0.2 wt.% sample but there are a lot more visible characteristics and crack lines in the 0.2 and 1.0 wt. % graphene-epoxy samples compared to unmodified or modified samples.

All these SEM images confirm that addition of more graphene nanoplatelets or modifying

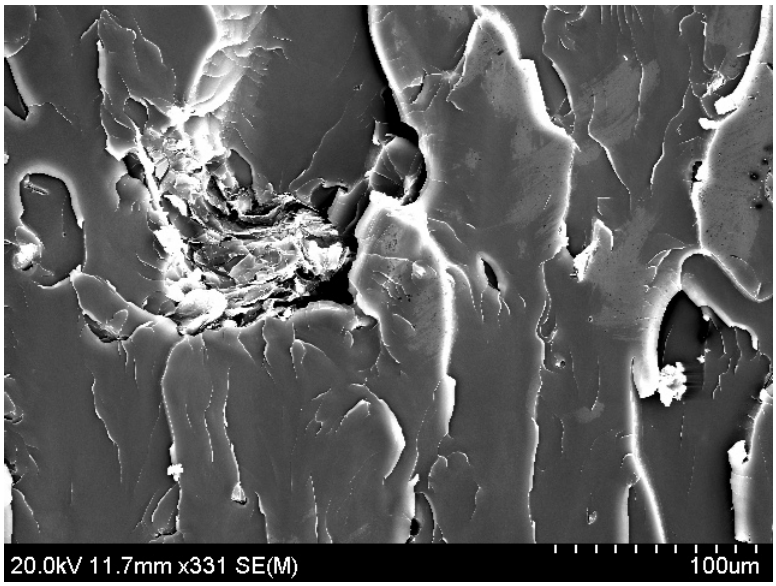


Figure 5: SEM of 0.2 wt.% unmodified graphene-epoxy

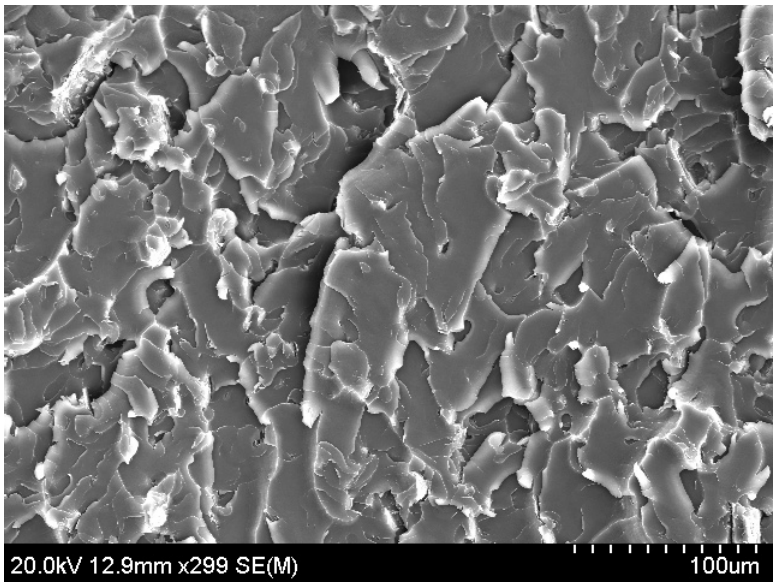


Figure 6: SEM of 1.0 wt.% unmodified graphene-epoxy

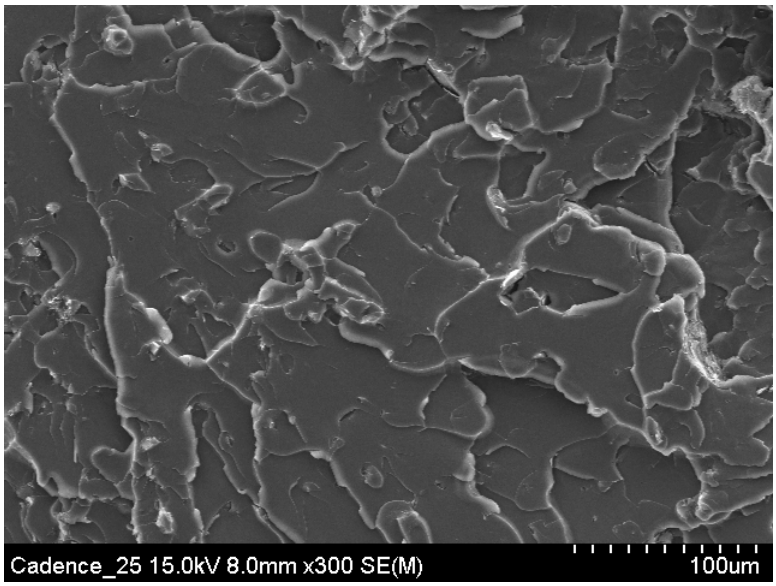


Figure 7: SEM of 0.2 wt.% GPTMS graphene-epoxy

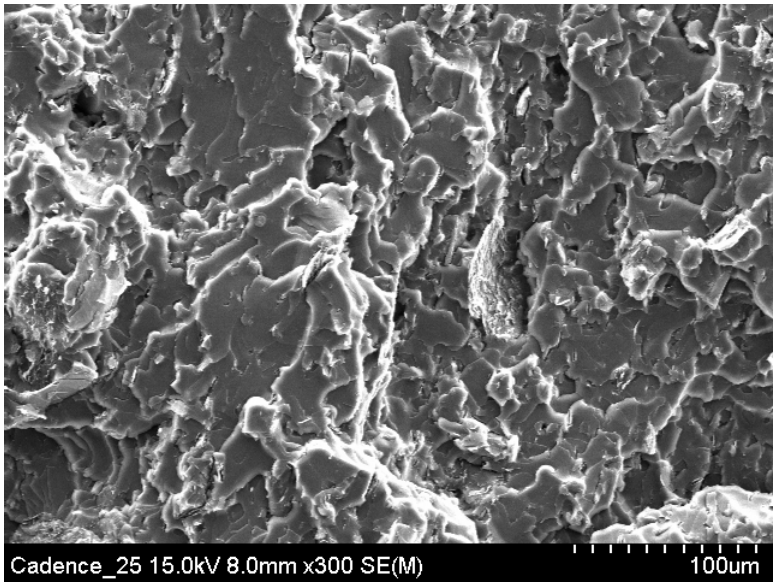


Figure 8: SEM of 1.0 wt.% GPTMS graphene-epoxy

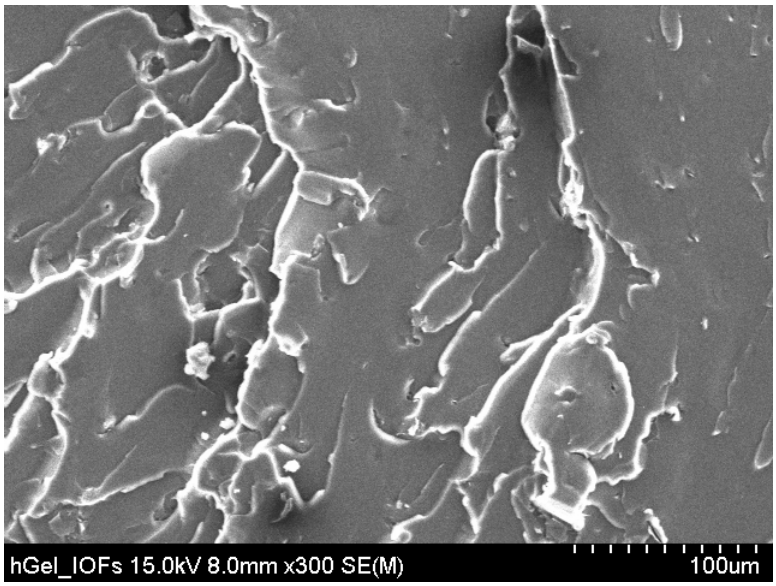


Figure 9: SEM of 0.2 wt.% modified graphene-epoxy

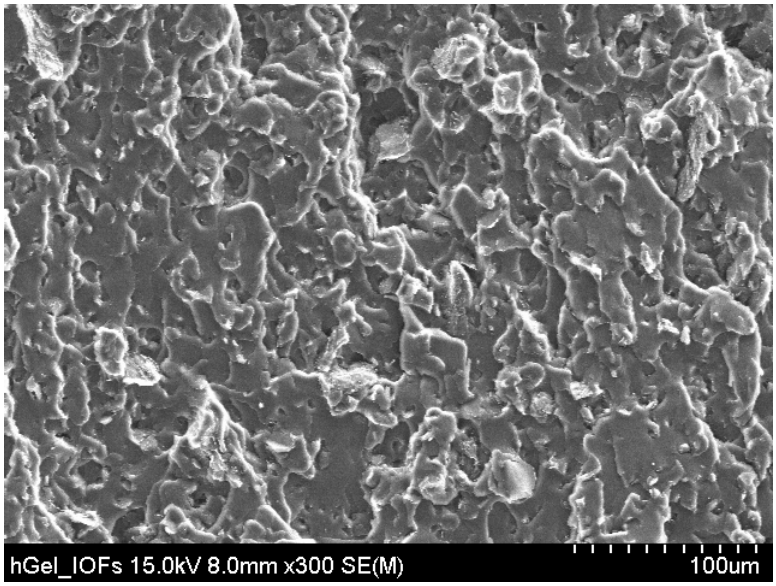


Figure 10: SEM of 1.0 wt.% modified graphene-epoxy

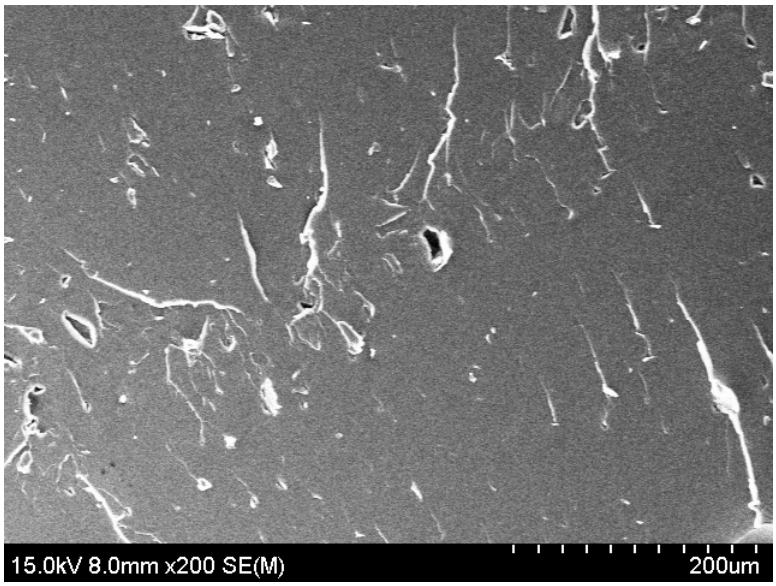


Figure 11: SEM of 0.2 wt.% APTMS graphene-epoxy

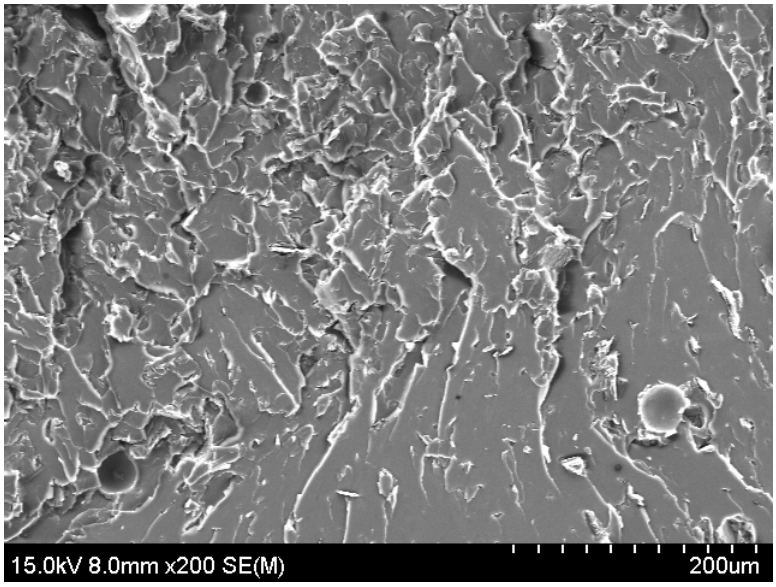


Figure 12: SEM of 1.0 wt.% APTMS graphene-epoxy

graphene nanoplatelets or using some form of dispersion technique for incorporating the graphene nanoplatelets in the epoxy matrix leads to the formation of more torturous crack paths when fracture toughness tests are performed. All these graphene nanoplatelets act as a barrier that prevent the crack from growing and just passing through the specimen. Better interfacial bonding between the graphene nanoplatelets and the epoxy and improved dispersion of graphene nanoplatelets in the epoxy is evident from a more rough crack surface.

When the graphene nanoplatelets are well dispersed in the sample, the cracks that are trying to propagate through the sample while fracture toughness test is in progress are met with more obstruction by the graphene nanoplatelets when compared to poorly dispersed graphene-epoxy samples. This is seen in the SEM images. More evenly distributed graphene nanoplatelets in the sample means more torturous paths for the cracks and thus leads to more characteristics in the image. In case of unmodified samples even though graphene nanoplatelets loading is increased, it can be seen that simply by increasing the amount of graphene nanoplatelets in the sample, the cracks can not be prevented from propagating easily through the sample. These unmodified samples do not show as much of torturous path or characteristics as is seen in case of modified samples. In those cases, both at higher and lower loadings, it has more characteristics and more crack paths.

3.3 Fourier-Transform Infrared Spectroscopy

Fourier-Transform Infrared Spectroscopy or FTIR was performed on as received graphene nanoplatelets, GPTMS functionalized graphene nanoplatelets and APTMS functionalized graphene nanoplatelets. Comparing the different FTIR spectra revealed interesting information.

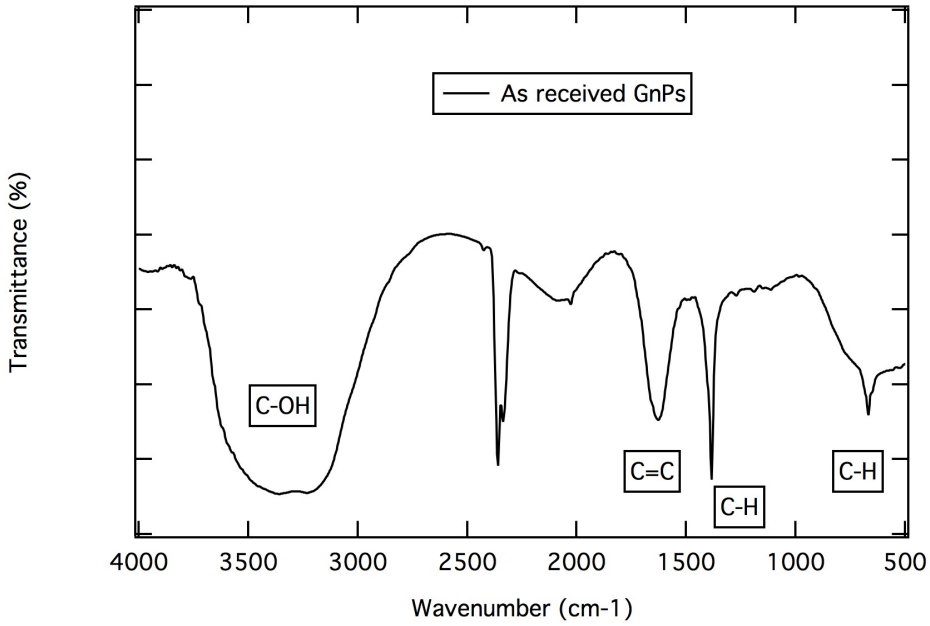


Figure 13: FTIR spectra of as received graphene nanoplatelets

Figure 13 shows the FTIR spectra of as received graphene nanoplatelets. FTIR was performed on solid powdered graphene nanoplatelets which were taken straight out of the box as supplied by the manufacturer. These graphene nanoplatelets were not processed or modified in any way after they were taken out of the box. Prominent peaks can be observed at 3300, 2400, 1600, 1400 and 600 cm-1 wavenumbers.

The peak at 3200 denotes the C-OH functional group, peak at 2400 residual carbon dioxide in the FTIR processing chamber, peak at 1600 denotes the C=C bonds, peak at 1400 denote the C-H bond and the peak at 600 denotes C-H stretching.

C=C peaks confirm that it has those bonds and also that it is a carbon allotrope. The other primary peaks confirm the presence of functional groups on the surface on the graphene nanoplatelets. The main functional group that is present is the -OH or the hydroxyl functional group. This also goes to show that although the manufactures claim that the graphene nanoplatelets are very pristine, it still does contain functional groups on the surface. These functional groups are actually beneficial in forming bonds with the epoxy and other solvents or surfactants which leads to better cross-linking and stronger networks.

The FTIR spectra of as received GPTMS was obtained from the supplier of GPTMS, i.e., Sigma Aldrich.

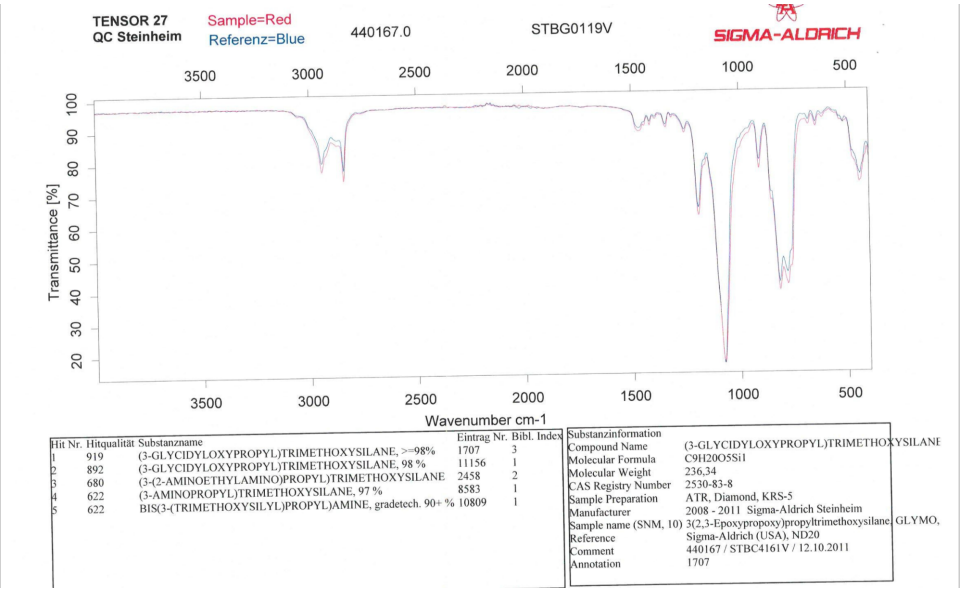


Figure 14: FTIR spectra of as received GPTMS

When Fourier-Transform Infrared Spectroscopy or FTIR was performed on GPTMS grafted graphene nanoplatelets and APTMS grafted graphene nanoplatelets. The different FTIR spectra of graphene nanoplatelets, GPTMS and GPTMS functionalized graphene nanoplatelets were compared in order to understand the effects of functionalization and also to study the differences between them.

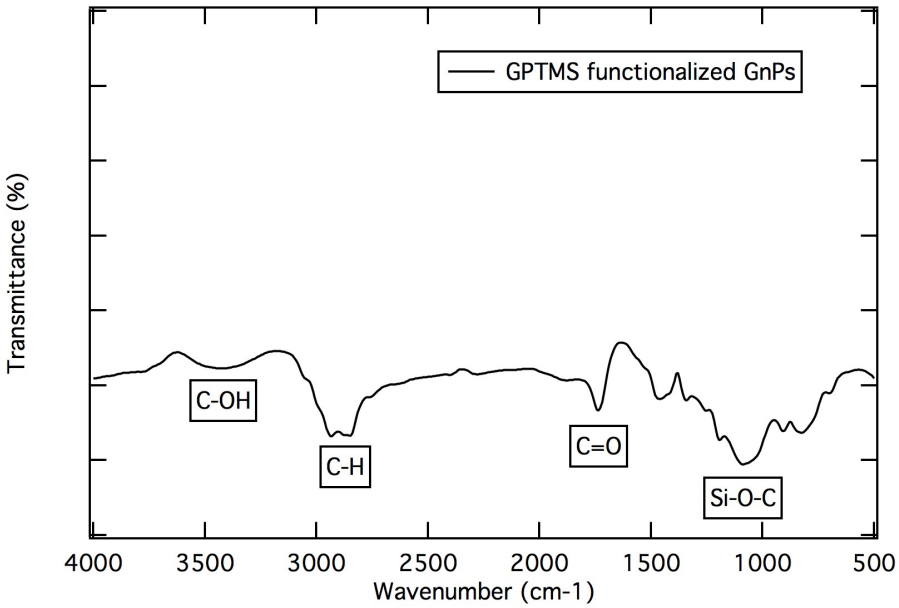


Figure 15: FTIR spectra of GPTMS functionalized graphene nanoplatelets

Figure 15 shows the FTIR plot of GPTMS functionaized graphene nanoplatelets. The graphene nanoplatelets were left to dry after the dispersion and functionalization technique and then FTIR was carried on those. In this FTIR spectra we can see peaks at around 1100, 1700, 2800, 2900 and 3400 cm-1 wavenumbers. The band at 3400 became has less pronounced peaks and is more flat now. It still corresponds to the -OH groups. So the peaks around 3200 denotes the C-OH functional group, peak at 2400 denotes the C-H bonds, peak at 1700 denotes the C=0 bonds. The bands at 1200 denote the presence of Si-O-C bonds. The presence of these peaks might not be conclusive that chemical reaction has taken place or not but definitely some chemical interaction has taken place. At least the silane molecules are still present in the system along with the graphene nanoplatelets and the chemical interaction might not be that strong due to the fact that these are 99% pristine graphene nanoplatelets and these graphene nanoplatelets just don't have enough active sites on their surface to form successful chemical bonds with the silane.

In case of the as received GPTMS, prominent peaks can be seen at 700 cm-1 and 1100 cm-1. When GPTMS is mixed with graphene nanoplatelets, we can still see peaks in those regions. The peaks at 3400 for as received graphene nanoplatelets have shifted after mixing and are less pronounced. This means that some form of interaction between the graphene nanoplatelets and the GPTMS molecules has taken place has taken place.

The FTIR spectra of as received APTMS was obtained from the supplier of APTMS, i.e., Sigma Aldrich.

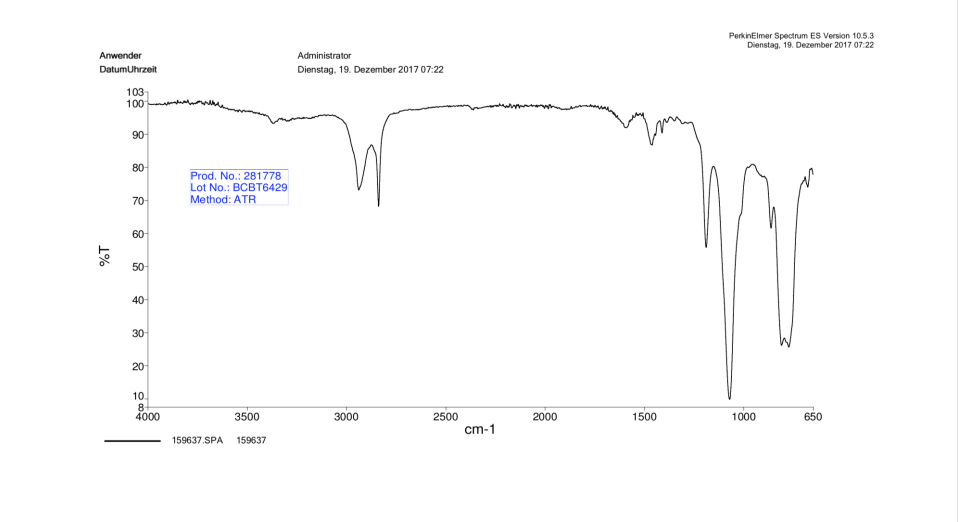


Figure 16: FTIR spectra of as received APTMS

When Fourier-Transform Infrared Spectroscopy or FTIR was performed on as received graphene nanoplatelets, GPTMS functionalized graphene nanoplatelets and APTMS functionalized graphene nanoplatelets. Comparing the different FTIR plots revealed interesting information.

Figure 17 shows the FTIR plot of APTMS functionalized graphene nanoplatelets. The graphene nanoplatelets were left to dry after the dispersion and functionalization technique and then FTIR was carried on those. In this FTIR spectra we can see peaks at around 1100, 1600, 2400 and 3400 cm-1 wavenumbers. The band at 3400 became has less pronounced

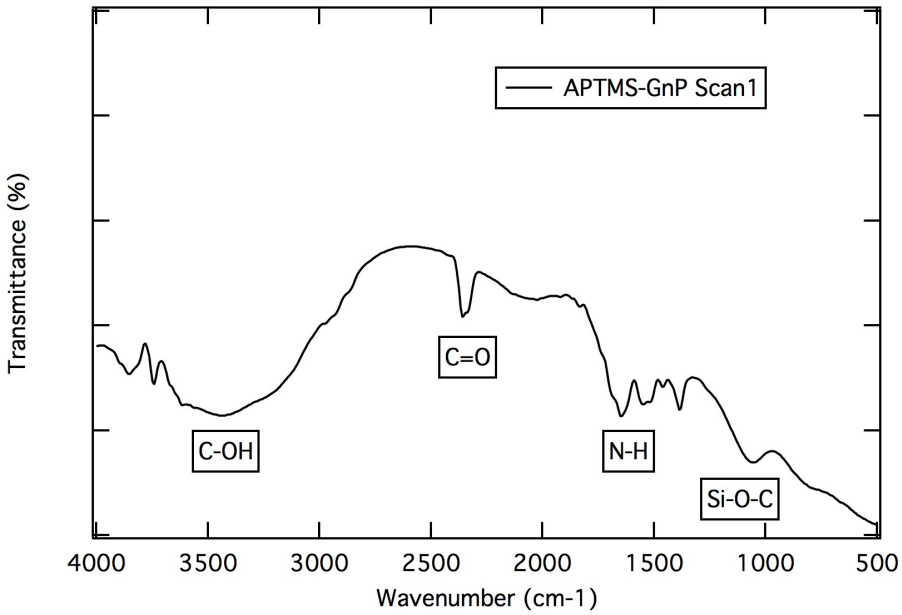


Figure 17: FTIR spectra of APTMS functionalized graphene nanoplatelets

peaks and is more flat now. It still corresponds to the -OH groups. So the peaks around 3200 denotes the C-OH functional group, peak at 2400 denotes the C=O bonds, peak at 1600 denotes the N-H bonds. The bands at 1100 denote the presence of Si-O-C and Si-O-Si bonds. This indicates that some form of chemical interaction is taking place.

As received APTMS has strong peaks because of the amine groups. Those are still present in the APTMS functionalized graphene nanoplatelets samples but shift in peaks and broader peaks can be seen after they have have been mixed.

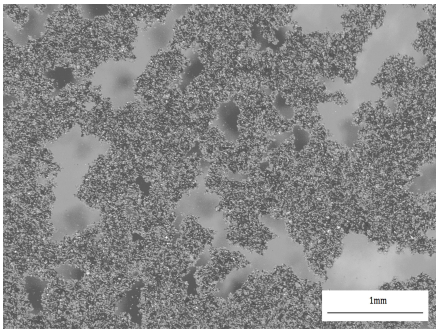
When comparing the FTIR plots of as received graphene nanoplatelets and APTMS and GPTMS functionalized graphene nanoplatelets samples separately we can see the appearance of certain peaks and changes in other peaks which can lead to the inference that the GPTMS and APTMS molecules are interacting with the graphene nanoplatelets and are at least grafting on to the surface of the graphene nanoplatelets if not chemically interacting. This is once again due to the fact that the graphene nanoplatelets used in this study are

99% pristine. So it's not unusual in this case to not observe strong peaks corresponding to the chemical interaction between the silanes and the graphene nanoplatelets because the chemical interactions are going to be weaker compared to graphene nanoplatelets with more active sites.

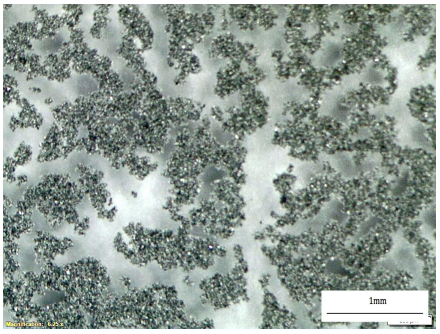
Also organic chemicals show sharper peaks in FTIR in general when compared to powdered samples like graphene nanoplatelets. This is why sharper peaks are observed for as received chemicals just by itself when compared to as received graphene nanoplatelets or when GnPs are functionalized with the silanes separately.

3.4 Transmission Optical Microscopy

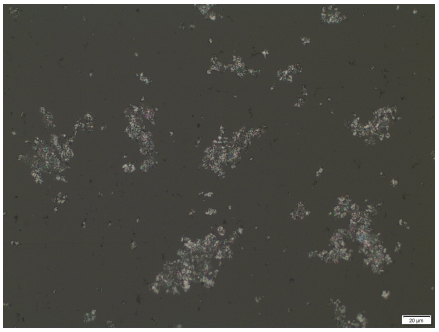
Transmission optical microscopy (TOM) was performed on graphene nanoplatelets (GnP) using standard dispersion technique and modified dispersion techniques.



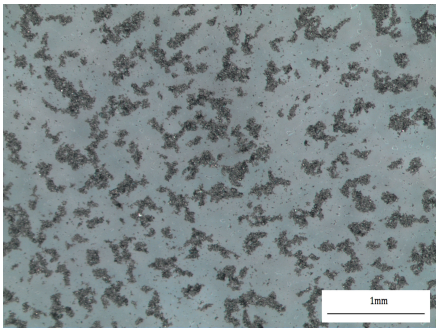
(a) GnP+IPA



(b) BM GnP+IPA



(c) BM GnP+IPA+US



(d) BM GnP+IPA+TX100+US

Figure 18: TOM images of GnPs dispersed using different techniques

Figure 18 shows the TOM images of graphene nanoplatelets on a glass slide which were dispersed using different techniques. In Figure 18a as received graphene nanoplatelets were dispersed only in a solvent, isopropyl alcohol (IPA). No other mechanical mixing process or chemicals were used. From the image it can be seen that the graphene nanoplatelets are not well distributed or dispersed in the solvent and they form aggregates. These visible agglomerations are the reason behind the low load bearing capacity of the samples once the composite is formed and failure at low loads means lower fracture toughness values which is not desirable at all for this study. This is not preferred for achieving good dispersion in

a sample so the process was modified. In Figure 18b as received graphene nanoplatelets were first ball milled and then added to IPA. The result is slightly improved and well dispersed graphene nanoplatelets in the medium but agglomerations are still there. These agglomerations will act as critical sites of failure in time when the composites are ready for testing. In Figure 18c the same process was used as the previous one but this time the ball milled graphene nanoplatelets were incorporated into the IPA using ultrasonication. This results in a slightly better distribution of graphene nanoplatelets in the medium and less aggregation sites than the previous ones but aggregates are still present. In Figure 18d the same technique was used but this time ultrasonication of the whole system was performed when ball milled graphene nanoplatelets were incorporated in the solvent in presence of the surfactant, Triton X-100. This results in a much better dispersion and almost no aggregations are to be found. This is because when Triton X-100 molecules are present in the system and the sample is ultrasonicated, the high energy ultrasonic waves break up the graphene nanoplatelets agglomerates and the space left behind by the separated GnPs is taken up by the big organic Triton X-100 molecules with long hydrophobic tails. These big organic molecules sheath between the layers of graphene nanoplatelets while keeping them separated from each other and preventing them from re-agglomerating. This phenomenon occurs with every ultrasonic wave passing through the sample and after a certain amount of time the graphene nanoplatelets are far away and separated enough. This is why this technique works best in the sample preparation process because it is successful in uniform dispersion of graphene nanoplatelets in the system. This also proves that the dispersion technique involving mechanical mixing processes like ultrasonication and ball milling and the use of surfactant, Triton X-100 works best for dispersing graphene nanoplatelets in a medium.

CHAPTER IV

CONCLUSION

In this experiment four different dispersion techniques were used to disperse graphene nanoplatelets into epoxy resin. The different processing techniques involved mechanical mixing, use of solvents, use of surfactants and use of silanes for chemical functionalization. The factors that dominate the mechanical properties of graphene-epoxy nanocomposites are the degree of dispersion of the graphene nanoplatelets in the epoxy resin and the interaction between the graphene nanoplatelets and the epoxy resin. Developing and improving these two factors were the main objective of this investigation. After all the different types of processing techniques were implemented, the fracture toughness of the prepared graphene-epoxy nanocomposites was studied. It was observed that in general fracture toughness values improved with improvement in dispersion techniques and with addition of graphene nanoplatelets to the epoxy but to a certain point. In case of unmodified graphene-epoxy samples, the peak fracture toughness values were obtained at 0.5 wt.% graphene nanoplatelets loading. This trend was also observed for graphene-epoxy samples prepared using both first and second type of dispersion techniques. Things started to change after the third dispersion technique was used. For samples prepared using the third modification technique the highest fracture toughness values were obtained for 2.0 wt.% graphene nanoplatelets loading and at 1.0 wt.% while using the two different types of silanes along with the third modification technique.

4.1 Summary

The peak value for samples prepared using third modification technique showed 130.9% increase in fracture toughness values when compared to neat epoxy. The peak value for samples prepared using GPTMS and the final modification technique showed 124.3% increase in fracture toughness values when compared to neat epoxy. The peak value for samples prepared using APTMS and third modification technique showed 140.9% increase in fracture toughness values when compared to neat epoxy. The final modification technique included ball milling, use of solvent (IPA) and surfactant (Triton X-100) which led to the optimum dispersion of graphene nanoplatelets in the epoxy resin.

Scanning electron microscopy was used to observe the fractured surface of the graphene-epoxy nanocomposites after the fracture experiment. Presence of crack lines, cracks with rough surface and increased surface characteristics validates the toughening mechanism of epoxy by incorporation of graphene nanoplatelets. By comparing the fractured surfaces of different samples, it can be concluded that the samples processed using the third modification technique along with GPTMS and APTMS had more crack characteristics even at higher loading when compared to unmodified samples and also for samples prepared using first and second modification technique. FTIR of silane added graphene nanoplatelets also showed the presence of Si-O-Si bonds, Si-O-C bonds and N-H bonds proving that silanization was successful to an extent. It would be possible to see more changes in FTIR if it was graphene oxide (GO) but since the graphene nanoplatelets used in this experiments are 99.5% pristine, these graphene nanoplatelets don't have abundant active sites where other chemicals can interact with it.

Overall this shows that out of all the different processing techniques used for preparing graphene-epoxy nanocomposites, the third modification technique including ball milling,

ultrasonication, use of solvents, use of surfactants and use of a silane, APTMS provided the best dispersion of graphene nanoplatelets in the epoxy resin and also the best interaction between the graphene nanoplatelets and the epoxy which led to superior fracture toughness values over the others.

4.2 Conclusion

Comparing the fracture toughness values of the different types of nanocomposites prepared and tested in this study it can be concluded that the third modification technique included ball milling, use of solvents and Triton X-100 (surfactant) led to the optimum dispersion of graphene nanoplatelets in the epoxy resin. The results were even better at higher graphene nanoplatelets loadings when compared to unmodified or other samples prepared using other methods. This is because ball milling separated the graphene nanoplatelets and Triton X-100 prevented the graphene nanoplatelets from re-agglomeration in the epoxy throughout the graphene nanoplatelets loading range. Without the use of mechanical dispersion techniques like Ball milling or surfactants like Triton X-100, it is not possible to prevent the graphene nanoplatelets from re-agglomeration. Ball milling is a high energy mechanical mixing process which separates the graphene nanoplatelets thus breaking up the agglomerates. Triton X-100 on the other hand is a surfactant with a very long organic polymer chain attached to it which is a hydrophilic tail and this big organic molecule goes between the graphene nanoplatelets and keeps the graphene nanoplatelets separated and thereby preventing the graphene nanoplatelets from forming agglomerates in the epoxy resin. This occurs especially when the surfactant Triton X-100 is present in the medium while ultrasonication. With every ultrasonic wave passing through the sample, it separates the graphene nanoplatelets and the big organic molecule of Triton X-100 fills the gap between the graphene nanoplatelets. These big organic Triton X-100 molecules keep the

graphene nanoplatelets away from each other and helps in better distribution of graphene nanoplatelets in the epoxy matrix by preventing their agglomeration. An optimum time duration of ultrasonication is enough to keep the graphene nanoplatelets separated in the system without damaging the graphene nanoplatelets or the epoxy or the Triton X-100 as ultrasonication is a high energy process and prolonged durations of this process could eventually damage all components in the composite involved. And comparing the fracture toughness values of these samples with other samples make it very clear that no matter what silane is added after this step, it doesn't improve the fracture toughness values. Addition of silanes does not show any more significant improvement in fracture toughness over samples dispersed using the above mentioned steps. This could be due to a number of reasons. First of all, more studies need to performed on what type of silane would work best with this specific combination of type of graphene nanoplatelets and epoxy resin used in this study. The graphene nanoplatelets used in this study are pristine graphene nanoplatelets or 99% graphene nanoplatelets. This is one of the purest form of graphene nanoplatelets available in the market and it is devoid of impurities and defects. What that means is that these graphene nanoplatelets do not have many active sites on its surface where chemicals like silanes can bond or attach or interact with these. The more the number of active sites on the surface of the graphene nanoplatelets, the better and easier it is for other chemicals to interact with it. These active sites on the surface of the graphene nanoplatelets consist of functional groups and free radicals which can form bonds with different types of organic chemicals like silanes. But since in this study the graphene nanoplatelets that are used are 99% pristine, there are very few to none active sites on their surface and this significantly affects the interaction of these graphene nanoplatelets with the silanes which are large organic molecules with functional groups. The silanes used might not be best suited for this

graphene-epoxy combination and further studies may reveal other better silanes that might improve the fracture toughness values over the Triton X-100 samples. Also the processing of silane functionalized graphene nanoplatelets might have some issues with it and might be reason behind not showing any major improvement in fracture toughness values over the Triton X-100 samples. It could also be due to the fact that there might be certain minor chemical interactions going on in the system when silanes are introduced in the presence of epoxy and Triton X-100. These chemical interactions which could be minor or significant could play some role in hindering the improved expected results. Some more detailed chemistry work might be required to fully understand and explain the phenomenon going on in the system while all those chemicals are in play. The only reason behind the silane functionalized graphene nanoplatelets showing good fracture toughness values is because these sample were still processed using ball milling and Triton X-100 and thus the graphene nanoplatelets are already well dispersed and some minor graphene nanoplatelets-silane interaction might be taking place on the surface of the graphene nanoplatelets with the help of the few active sites that are present. This graphene nanoplatelets-silane interaction might not be good enough or significant enough to result in much higher fracture toughness values over the ball milled and Triton X-100 samples but at least it doesn't lower the fracture toughness values. So overall in this study, it can be noted that ball milling, ultrasonication, use of Triton X-100 as a surfactant has positive and significant impacts in improving the fracture toughness values of graphene-epoxy composites. The silanes GPTMS and APTMS on the other hand do not affect the fracture toughness values of graphene-epoxy composites when used alongside the dispersion techniques involving ball milling, ultrasonication and Triton X-100 as a surfactant.

4.3 Recommendations

This study has mainly focussed on the fracture toughness of graphene-epoxy nanocomposites. Some further studies in this area could be -

- The effects of adding more than 2 wt.% graphene nanoplatelets in epoxy on fracture toughness should be studied as this study only focussed on a specific range of graphene nanoplatelets loading of 0.1 wt.% to 2.0 wt.%.
- In this study only fracture toughness was studied as a mechanical property of the material. Studying other mechanical properties that has not been studied before but using these current techniques can lead to important findings.
- This study only focussed on the mechanical aspect of the nanocomposite. Studying thermal and electrical properties of graphene-epoxy composites is important for assessing the multi-functional properties of the composites.
- The surfactant used in this work is Triton X-100 and it worked pretty well but finding more impactful surfactants and coupling agents could be useful.
- Pristine 99% pure graphene nanoplatelets were used for the experiments of this work. Studying the effects of techniques used in this study on other types of graphene is also important.
- Performing Thermogravimetric analysis of EPON 862 epoxy resin and the composite could lead to more information about the epoxy used.
- Dispersion techniques and interaction of graphene nanoplatelets with epoxy and other chemicals was studied but another way of achieving higher fracture toughness values is by changing the orientation of graphene nanoplatelets in the epoxy matrix.

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